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## BOND DISSOCIATION ENERGIES BY KINETIC METHODS

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### I. INTRODUCTION

The main aim of this review is to present an assessment of bond dissociation energies, which have recently been revised or determined for the first time by kinetic

methods. The review is therefore centered on polyatomic molecules. Szwarc (180) dealt in detail with the methods for obtaining bond dissociation energies in the first major review of the field, and Cottrell (50) again covered the whole subject in his monograph. It

will suffice here to deal only with modifications and expansions of the methods which have been developed over the past few years.

Sehon and Szwarc (169) brought Szwarc's earlier review up to date in 1957. An account of dissociation energies in small hydrocarbon molecules and their fragments (121) appeared in 1961, but the "best" values proposed then are substantially in need of revision. A short book (142) was published in 1962, and, although it deals with some aspects of bond dissociation energies by kinetic methods, it was written mainly from the point of view of the thermochemist. While the present review was being prepared Benson (23) published a review article entitled "Bond Energies." This is an excellent account of definitions, background information, experimental methods, and topics related to bond dissociation energies. It was written, however, from a standpoint entirely different from that adopted here, and does not set out to discuss the merits of the various determinations of specific bond dissociation energies, giving mainly collective references. Nevertheless, it is pleasing to note that the results tabulated by Benson for bond dissociation energies in polyatomic molecules are in substantial agreement with those now being proposed.

As indicated by the title it is not the present purpose to cover all aspects of the subject. Electron impact studies on bond dissociation energies in polyatomic molecules, which on the whole are less reliable than kinetic determinations, will only be considered where they are relevant to kinetic results. No attempt has been made to present a historical account. In cases where a value has been in dispute over a period of many years, discussion is initiated with a recent reference which summarizes the early data. Most of the values considered have appeared in the literature between 1958 and September 1965, although some earlier values are included where they are still thought to be reliable.

## II. DEFINITIONS AND CONVENTIONS

The bond dissociation energy or bond strength of a chemical bond A-B is usually taken to mean the enthalpy change of the reaction



in the ideal gas state, and is given by

$$D(A-B) = \Delta H_1^\circ = \Delta H_f^\circ(A) + \Delta H_f^\circ(B) - \Delta H_f^\circ(AB) \quad (\text{Eq 2})$$

Bond dissociation energies in polyatomic molecules are referred to 298°K ( $D_{298}$ ) since this is a standard temperature for thermodynamic data. Corrections to results obtained at other temperatures are usually small and are sometimes neglected when the accuracy of the determination is low. For determinations where the precision is high, such as  $D(C-H)$  values in

the lower alkanes, temperature corrections become important. In these cases it is usually assumed that the heat capacities of the alkyl radicals are identical with those of their parent hydrocarbons and the temperature correction is then obtained from Kirchoff's equation. The heats of formation of gaseous elements are often listed at 0°K, and these must also be corrected to 298°K for calculations involving polyatomic molecules. The relations between  $D_{298}$ , intermolecular forces, and other quantities have been discussed by Benson (23).

The determination of bond strengths and heats of formations of radicals are complementary problems since it follows from Eq 2 that  $D(A-B)$  can be calculated from the heats of formation of the radicals A and B and the heat of formation of the compound AB. This is often the only way of determining a value of  $D(A-B)$  and is particularly useful for bonds involving atoms (X), *i.e.*,  $D(A-X)$ , since the heats of formation of many atoms are known to  $\pm 0.1$  kcal or better, from spectroscopic studies. A short list of heats of formation of gaseous atoms used in this review is included in Table XXIX. The accuracy of bond dissociation energies calculated from Eq 2 is also dependent upon the determinations of the heats of formation of the compounds. These have been tabulated for most of the hydrocarbons (165) and for inorganic compounds and organic compounds containing less than three carbon atoms (164, 175). For larger organic molecules a comprehensive compilation of data is lacking, although oxygen-containing compounds are considered in a fairly recent review (84). References are given throughout this review for heats of formation of compounds not listed in the above sources. All heats of formation of compounds mentioned here refer to 298°K in the gas phase.

If reaction 1 involves 1 mole of reactant then the usual units of  $D(A-B)$  are kilocalories; this is implicit in all the reactions considered here. Since the review is concerned with bond dissociation energies from kinetic measurements of elementary reactions in the gas phase, the kinetic units and definitions are also important. Unimolecular rate constants will be considered in units of  $\text{sec}^{-1}$ , bimolecular rate constants in units of  $\text{mole}^{-1} \text{cc sec}^{-1}$ . The temperature dependence for the rate constant ( $k$ ) is assumed to obey the Arrhenius equation

$$\log k = \log A - (E/2.303RT)$$

where  $E$  is the Arrhenius activation energy (kcal) and  $A$  is a constant (same units as  $k$ ) known as the  $A$  factor or in unimolecular reactions as the frequency factor. Rate constants will be expressed in the form

$$\log k = \log A - (E/\theta)$$

where  $\theta = 2.303RT$  in kcal  $\text{mole}^{-1}$ , as suggested by Benson and DeMore (27).

It is important to distinguish between the bond dissociation energy or bond strength of a chemical bond, as defined above, and the term mean-bond energy ( $E$ ) frequently encountered in thermochemistry. The latter quantity applies to compounds of the general type  $AC_n$  and is defined from the equation

$$AC_n = A + nC$$

Hence

$$E(A-C) = \frac{1}{n}[\Delta H_f^\circ(A) + n\Delta H_f^\circ(C) - \Delta H_f^\circ(AC_n)] \quad (\text{Eq 3})$$

or in other words the average energy per bond required to dissociate the molecule into its constituent atoms. Mean-bond energies are often useful for thermochemical calculations but have no real physical significance. They usually have considerably different values from bond dissociation energies, as shown by the example of methane. Equation 3 gives for methane

$$E(C-H) = \frac{1}{4}[\Delta H_f^\circ(C) + 4\Delta H_f^\circ(H) - \Delta H_f^\circ(CH_4)]$$

and from enthalpy data at 298°K,  $E(C-H) = 99$  kcal. For the stepwise dissociation of methane, on the other hand, the bond dissociation energies are  $D(CH_3-H) = 104$ ,  $D(CH_2-H) = 104$ ,  $D(CH-H) = 108$ , and  $D(C-H) = 81$  kcal (section VA1).

### III. EXPERIMENTAL METHODS

#### A. PYROLYTIC REACTIONS

This method can be applied to unimolecular reactions involving a simple bond rupture as shown in Eq 1. The enthalpy change for this reaction is related to the activation energies ( $E_1$ ,  $E_{-1}$ ) of the forward and reverse reactions by the equation

$$\Delta H_1 = \Delta E + RT = (E_1 - E_{-1}) + RT$$

The  $RT$  term allows for the change in the number of moles, but this is approximately offset by the correction which should be applied to  $E_1$  to bring it to 298°K, since pyrolyses are carried out at temperatures well above 298°K. Hence the equation becomes

$$\Delta H_1 \cong E_1 - E_{-1}$$

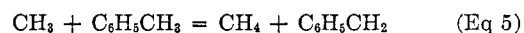
The reverse of Eq 1 is a radical-radical combination reaction for which it is usually assumed that the activation energy is zero. There is now a considerable body of direct experimental evidence, from rotating sector work on the combination of like radicals (111, 138, 139) and indirect evidence from cross-combinations of unlike radicals (111), to justify the assumption  $E_{-1} = 0$ . The enthalpy change  $\Delta H_1$ , which defines  $D_{298}(A-B)$ , is thus given directly by  $E_1$ .

The experimental problem is then to determine ac-

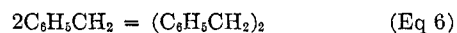
tivation energies of decomposition reactions. Most of the accepted bond dissociation energies from pyrolyses have been derived from flow experiments, which overcome the disadvantage of complicating side reactions that beset measurements in static systems. The most widely applied flow system is the toluene-carrier technique developed by Szwarc (180) and recently modified by replacing toluene with aniline (55, 56). The essential feature of the toluene-carrier system consists of passing the compound under investigation through a high-temperature furnace in a stream of toluene. The bond being studied should be considerably weaker than the weakest bond in toluene, *i.e.*,  $D(C_6H_5-CH_2-H) = 85$  kcal, and in practice a bond strength of 70 kcal is about the maximum which can be determined. The method will be illustrated by the pyrolysis of cumene where the reaction of interest is



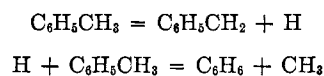
In the presence of a large excess of toluene the highly reactive methyl radicals are removed from the system by the reaction



Chain reactions are prevented since the benzyl radicals, which are resonance stabilized and much less reactive than methyl, eventually dimerize outside the reaction zone



A major drawback to the use of toluene, however, is that at higher temperatures the following reactions occur



The additional source of methyl radicals, and hence methane *via* Eq 5, can make studies of the pyrolyses of compounds containing labile R-CH<sub>3</sub> bonds ambiguous. This problem has been overcome by substituting aniline for toluene. The reaction system for cumene, decomposed by the aniline-carrier technique, is then identical with that for toluene with the anilino radical,  $C_6H_5NH$ , replacing the benzyl radical. The validity of the proposed mechanism with aniline has been checked by obtaining identical rate constants with both carrier gases. Disadvantages of aniline, such as its low volatility and the difficulty of freeing it from dissolved gases, are not serious.

The detailed application of the aniline-carrier method can be illustrated by further consideration of the decomposition of cumene. It is initially required to determine the unimolecular rate constant ( $k_d$ ) for reaction 4. This is best done by measuring the amount of methane formed, which is the exclusive product of the methyl radicals from the decomposition. The rate

constant is then calculated from the first-order equation

$$k_t = \frac{1}{t} \ln \frac{a}{a-x}$$

where  $t$  is the contact time derived from the flow constants of the apparatus,  $a$  is the amount of cumene passed through the furnace during the run, and  $x$  is the amount of methane determined by analysis. It is also possible to follow the decomposition by measuring the amount of dibenzyl (toluene carrier) or hydrazobenzene (aniline carrier) formed in reaction 6. With the advent of improved analytical techniques, particularly gas chromatography, the analysis of dibenzyl has lost favor to analyzing the product from the reactive radical produced in the initial decomposition. It is important that the rate constants be shown to be independent of contact time, partial pressure of reactant in the carrier gas, and surface-to-volume ratio of the reaction vessel, to establish that the reaction is truly unimolecular and homogeneous. The activation energy is then obtained from an Arrhenius treatment of the rate constants determined over the widest range of temperatures possible. The technique is particularly suitable for studying decompositions which give rise to a resonance-stabilized radical (S) as well as a reactive radical (R). The bonds in such compounds (S-R) are considerably weakened by the effect of resonance, thereby avoiding the necessity of a high-temperature study. At the same time the mechanism is simplified as there is only one reactive radical.

Recent studies both by the toluene- and aniline-carrier techniques (108, 109) have shown that the results on the decompositions of small molecules are sometimes misleading. In the range of pressures available for carrier experiments, the rates of decomposition of these molecules can be affected by the over-all pressure in the system, as predicted by the theories of unimolecular reactions. Accordingly the activation energy observed experimentally in the pressure fall-off region may be several kcal less than the limiting-pressure activation energy ( $E_\infty$ ) which is identified with the bond dissociation energy. Generally the study of pressure effects on first-order rate constants is not readily achieved in toluene- or aniline-carrier experiments, although a recent study (206) of the decomposition of ethyl iodide has been partially effective in this direction.

As previously mentioned the temperature dependence of the rate constant is assumed to follow the Arrhenius equation

$$\log k = \log A - (E/\theta)$$

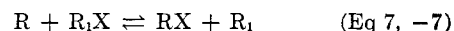
Clearly the value of the  $A$  factor for the decomposition reaction is of fundamental importance since its prior knowledge can lead to a value of the activation energy merely from the measurement of the rate constant at one

temperature. Szwarc (180) placed much emphasis on the "normal"  $A$  factor in a pyrolytic reaction being close to  $10^{13} \text{ sec}^{-1}$ , *i.e.*, of the same order as a vibrational frequency. Indeed at the time the experimental results largely justified this assumption. An overwhelming mass of data on unimolecular reactions has now accumulated in which the  $A$  factors are many powers of ten higher than  $10^{13} \text{ sec}^{-1}$ . The question of "normal" and "high"  $A$  factors has been treated at length by Gowenlock (75). More recently it has been concluded (27), as a general rule, that bond rupture to give two large radicals results in an  $A$  factor in the range  $10^{15}$  to  $10^{18} \text{ sec}^{-1}$ , while decompositions to give an atom and a radical have  $A$  factors of the order of  $10^{14}$  to  $10^{15} \text{ sec}^{-1}$ . High  $A$  factors are taken to indicate a "loose" transition state with a large degree of free rotation between the resulting fragments. Steel and Laidler (174) have put forward theoretical arguments to account for high  $A$  factors in unimolecular reactions. It is now apparent that there is no reason for assuming a constancy of  $A$  factor for unimolecular reactions. Accordingly, there is no justification for Szwarc's method of determining relative rate constants for a series of related decompositions, and hence differences in bond dissociation energies, on the basis of a constant  $A$  factor. Results obtained by this method and summarized by Trotman-Dickenson (191) are not considered here. Benson and Buss (25) criticized the early results on the decomposition of toluene itself by the flow method on the grounds of an oversimplified mechanism, and this has often been accepted as a general criticism of the pyrolytic method. From the increasing body of self-consistent data accumulated by the toluene- and aniline-carrier techniques and from the fact that the pyrolysis of toluene is a particularly difficult case, it appears that these criticisms are not generally applicable.

In conclusion it may be said that carrier experiments can lead to reliable rate data and hence reliable bond dissociation energies provided (i) the mechanism is well established, (ii) the decomposition is not in the pressure-sensitive region, and (iii) there are no prior assumptions concerning the  $A$  factor of the decomposition.

## B. METATHETICAL REACTIONS

The same principle applies as for the pyrolytic method; the enthalpy change of a metathetical reaction involving a free radical is given by the difference in activation energies of the forward and reverse reactions. Hence for the generalized reactions



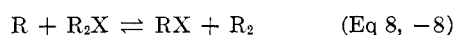
we have

$$\Delta H_{7,-7} = E_7 - E_{-7}$$

there being no change in the number of moles in the reaction. From the definition of bond dissociation energy it follows that

$$D(R_1-X) - D(R-X) = E_7 - E_{-7}$$

In other words, the difference in strengths between the bond broken and the bond formed is equal to the difference in activation energies of the forward and reverse reactions. If one of the bond dissociation energies is known, the other can thus be determined from the activation energy difference. Kistiakowsky and Van Artsdalen (118) were the first to exploit this general method which has subsequently been applied in many forms. Bond dissociation energies determined by this procedure are among the most reliable known for polyatomic molecules. The experiments are much easier to perform than pyrolytic flow reactions since they occur at considerably lower temperatures. The method is particularly suited to determining differences in bond dissociation energies in a series of related compounds. If in addition to reactions 7 and -7 the following reactions are considered.



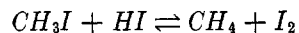
Then for the two pairs of reactions

$$D(R_1-X) - D(R_2-X) = (E_7 - E_{-7}) - (E_8 - E_{-8})$$

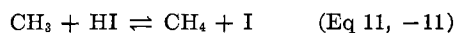
This difference in bond dissociation energies is not subject to any uncertainty in the value of  $D(R-X)$ .

There are many ways for measuring the activation energies of metathetical reactions of the type described above. In all cases different systems have to be devised for dealing with the forward and reverse reactions. It is important to realize that equilibrium is never established and that these are rate measurements and not thermodynamic equilibrium studies. To illustrate the versatility of the general procedure three specific examples are considered.

#### 1. Determination of $D(\text{CH}_3\text{-I})$ from Kinetic Measurements on the System



The reaction between methyl iodide and hydrogen iodide has recently been reexamined (64) by measuring the rate of iodine formation with a spectrophotometer. The above equation represents the over-all reaction, the stoichiometry of which was checked by the analysis of methane. The detailed mechanism involves the following atomic and free-radical reactions



From a steady-state treatment of this scheme the rate of formation of  $\text{I}_2$  is given by

$$R_{\text{I}_2} = (k_{10}k_{11}K_9^{1/2}[\text{RI}][\text{HI}][\text{I}_2]^{1/2}) / (k_{-10}[\text{I}_2] + k_{11}[\text{HI}]) \quad (\text{Eq 12})$$

where  $k$  = rate constant,  $K$  = equilibrium constant, and square brackets denote concentration. The rate of formation of iodine at any given time was obtained by drawing tangents to the iodine *vs.* time curves. The concentrations of iodine, methyl iodide, and hydrogen iodide were also obtained from these plots and the over-all stoichiometry of the reactions. Rearranging Eq 12 gives

$$\frac{[\text{I}_2]}{[\text{HI}]} = \frac{k_{10}k_{11}K_9^{1/2}[\text{RI}][\text{I}_2]^{1/2}}{k_{-10}R_{\text{I}_2}} - \frac{k_{11}}{k_{-10}}$$

so that by plotting  $[\text{I}_2]/[\text{HI}]$  *vs.*  $[\text{RI}][\text{I}_2]^{1/2}/R_{\text{I}_2}$ ,  $(k_{10}k_{11}K_9^{1/2})/k_{-10}$  is obtained from the slope and  $k_{11}/k_{-10}$  from the intercept.  $k_{10}$  follows from the known value of  $K_9$ .

An alternative procedure for calculating  $k_{10}$  consists of applying an integrated form of Eq 12. Although the resulting equation is insensitive to the data, expansions of the integrated equation fit the data well and lead to more accurate rate constants than the simple graphical method outlined above, which involves the errors associated with measuring tangents. The main point pertinent to the present purpose is that accurate values of  $k_{10}$  are obtained over a range of temperatures, and thus  $E_{10}$  is determined from an Arrhenius treatment. For reactions 10 and -10 the following relation applies

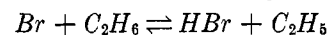
$$D(\text{CH}_3\text{-I}) - D(\text{I-I}) = E_{10} - E_{-10}$$

$E_{10}$  was found to be 20.5 kcal at about 558°K and was corrected to 20.2 kcal at 298°K.  $D(\text{I-I}) = 36.1$  kcal so that

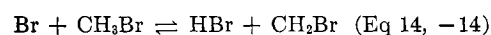
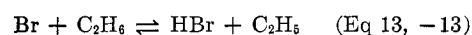
$$D(\text{CH}_3\text{-I}) = 36.1 + 20.2 - E_{-10}$$

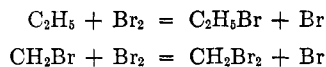
The activation energy ( $E_{-10}$ ) for the attack of methyl radicals on iodine has not been measured but there are strong indications that it must be very small and accordingly it has been assumed (72) to be zero to give  $D(\text{CH}_3\text{-I}) = 56.3$  kcal.

#### 2. Determination of $D(\text{C}_2\text{H}_5\text{-H})$ from Kinetic Measurements on the System



The first accurate kinetic measurements of reaction 13 were described by Andersen and Van Artsdalen (4). The system has subsequently been investigated by the competitive bromination technique (60) which has proved extremely useful in determining  $D(\text{C-H})$  values in alkanes. The general method can be illustrated by reference to ethane, where mixtures of ethane and methyl bromide were treated with bromine





For low percentage conversions of the reactants the following rate expression applies

$$k_{13}/k_{14} = \text{C}_2\text{H}_5\text{Br}[\text{CH}_3\text{Br}]/\text{CH}_2\text{Br}_2[\text{C}_2\text{H}_6]$$

where  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{CH}_2\text{Br}_2$  are the total amounts of alkyl bromides formed and  $[\text{C}_2\text{H}_6]$  and  $[\text{CH}_3\text{Br}]$  are the initial concentrations of reactants. Rate constant ratios were therefore obtained by analyzing for the bromides by gas chromatography, and from a knowledge of the initial ratio of reactant concentrations. The effects of the reverse reactions, -13 and -14, appear to cancel each other out as the rate constant ratios were not altered by the addition of relatively large amounts of hydrogen bromide. A series of determinations over a range of temperatures yielded

$$\log(k_{13}/k_{14}) = 0.135 + (2.65/\theta)$$

and hence  $E_{14} - E_{13}$  was deduced to be 2.65 kcal. The rate constant for reaction 14 had previously been found (118) to be

$$\log k_{14} = 13.73 - (16.05/\theta)$$

from which it follows that  $E_{13} = 13.40$  kcal.

For reactions 13 and -13 the following relation applies

$$D(\text{C}_2\text{H}_5\text{-H}) = D(\text{H-Br}) + E_{13} - E_{-13}$$

and therefore to obtain  $D(\text{C}_2\text{H}_5\text{-H})$ ,  $E_{-13}$  remains the only unknown. This difficulty was removed by Fettes and Trotman-Dickenson (61) who photolyzed methyl ethyl ketone in the presence of mixtures of hydrogen bromide and iodine and followed reactions -13 and



The products ethane and ethyl iodide were analyzed and the rate constant ratio was obtained from

$$k_{-13}/k_{15} = \text{C}_2\text{H}_6[\text{I}_2]/\text{C}_2\text{H}_5\text{I}[\text{HBr}]$$

From the temperature coefficient it was shown that

$$\log(k_{-13}/k_{15}) = 0.228 - (2.29/\theta)$$

and by making the reasonable assumption that  $E_{15} = 0$  it was deduced that  $E_{-13} = 2.29$  kcal. Hence it follows that at the mean experimental temperature of 460°K

$$D_{460}(\text{C}_2\text{H}_5\text{-H}) = D_{460}(\text{H-Br}) + 13.40 - 2.29 = 99.0$$

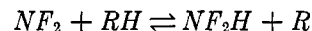
and

$$D_{298}(\text{C}_2\text{H}_5\text{-H}) = 98.2 \text{ kcal}$$

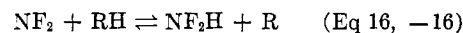
This general method has been successfully applied (60) to the reactions of bromine with methane, ethane, propane, *n*- and isobutane, neopentane, and methyl halides by reacting pairs of these substances with bro-

mine and referring the relative Arrhenius parameters to the previously known rate constant for the reaction of bromine with methyl bromide (118).

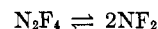
### 3. Confirmation of $D(\text{R-H})$ Values in Alkanes from Kinetics of the System



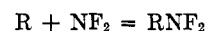
System 16, -16 illustrates a third approach for follow-



ing the kinetics of metathetical reactions of free radicals.  $\text{NF}_2$  radicals are conveniently produced *via* the equilibrium dissociation



since the N-N bond strength is only 20 kcal. Furthermore the concentrations of the radicals are readily calculated from the temperature and pressure in the system since the equilibrium constant has been accurately measured (104). When  $\text{N}_2\text{F}_4$ , or rather an equilibrium mixture consisting mainly of  $\text{NF}_2$ , is mixed with an alkane at a sufficiently high temperature, the alkane is consumed at a rate consistent with reaction 16. The resulting alkyl radicals presumably combine with further  $\text{NF}_2$  radicals, which are present in large excess



Unfortunately, the reaction cannot be followed by measuring the difluoramine products since these compounds are unstable. The measurement of the disappearance of the alkane, however, serves the same purpose, and this is achieved from a knowledge of the amount added at the start of an experiment and by analyzing the amount remaining at the end. The rate constants can be calculated from the second-order equation

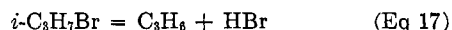
$$k_{16}t = 1/2[a - (b/2)]^{-1} \ln \{ [(a-x)/a] / [(b-2x)/b] \}$$

where  $t$  = run time,  $a$  = initial concentration of alkane,  $b$  = initial concentration of  $\text{NF}_2$  radicals, and  $x$  = concentration of alkane consumed. To check that the mechanism is valid the rate constants must be consistent over wide ranges of concentrations of both reactants, but as previously stated, with the  $\text{NF}_2$  always in considerable excess. This system has been successfully applied (85) to the reactions of  $\text{NF}_2$  radicals with *n*- and isobutane and cyclo- and neopentane. The activation energies are listed in Table I of section IV. Although the activation energies for the reverse reactions, -16, have not been determined and the value of  $D(\text{NF}_2\text{-H})$  is uncertain, the activation energies ( $E_{16}$ ) when plotted against the relevant  $D(\text{C-H})$  values in the alkanes yield a reasonable straight line. This is in accord with the Polanyi relation and may be taken as confirmation of the proposed  $D(\text{C-H})$  values. This point is discussed in more detail in section IV.

## C. SHOCK-TUBE REACTIONS

Reactions in shock tubes have sometimes proved useful in deciding between different values obtained spectroscopically for dissociation energies in diatomic molecules. The major advantages of the method are the high temperatures obtainable and the completely homogeneous reaction conditions, but against this must be set the difficulty of measuring the exact reaction temperature and exact reaction time. Bauer (17), Gaydon (67), and others have outlined the various conventional shock-tube techniques in relation to dissociation energies, and further elaboration would not seem justified here since there are very few dissociation energies which can be assigned with confidence from shock-tube studies.

An adaptation of the shock-tube procedure (195, 196) may prove to be more valuable. The method consists of carrying out comparative or competitive reactions involving pairs of reactants in a single-pulse shock tube, where one of the reactions, with previously established kinetics, serves as an internal thermometer and timing device. Dehydrohalogenation reactions were first studied with the decomposition of isopropyl bromide

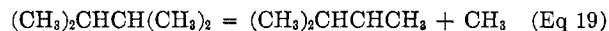
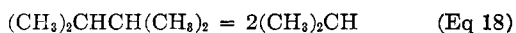


as the reference reaction. Mixtures of isopropyl bromide and another halide, greatly diluted with argon, were subjected to a shock-tube reaction and the dwell times ( $t$ ) obtained from the pressure history. The rate constant for the decomposition of each halide was then calculated from the equation

$$k = (1/t) \ln c_i/c_f$$

where  $c_i$  and  $c_f$  are the initial and final concentrations of the halides, respectively, determined by gas chromatographic analysis. Relative Arrhenius parameters can then be obtained by plotting  $\log k$  for  $i\text{-C}_3\text{H}_7\text{Br}$  against  $\log k$  for the other halide, over a range of temperatures. Absolute Arrhenius parameters for the decomposition of the second halide follow from the known rate constant for the decomposition of  $i\text{-C}_3\text{H}_7\text{Br}$ . The results for a series of dehydrohalogenation reactions are in excellent agreement with previous values obtained by conventional kinetic methods.

So far, the only radical elimination reaction studied by the new method has been the decomposition of 2,3-dimethylbutane, and the results look most encouraging (198). The reference reaction was the decyclization of cyclohexene for which the Arrhenius parameters were measured relative to the original standard, the decomposition of isopropyl bromide (197). The mechanism for the decomposition of 2,3-dimethylbutane is fairly complex but there are two initial decomposition reactions



for which the rate constants were found to be

$$\log k_{18} = 16.1 - (76.0/\theta)$$

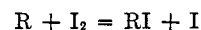
$$\log k_{19} = 16.6 - (81.1/\theta)$$

The activation energies  $E_{18} = 76.0$  and  $E_{19} = 81.1$  kcal can be equated to the bond dissociation energies  $D((\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)_2)$  and  $D((\text{CH}_3)_2\text{CHCH}(\text{CH}_3)-\text{CH}_3)$ , respectively, by making corrections to allow for the change in the number of moles and the mean temperature of the experiments of 1100°K. The values so obtained are  $D_{298}((\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)_2) \cong 77$  kcal and  $D_{298}((\text{CH}_3)_2\text{CHCH}(\text{CH}_3)-\text{CH}_3) \cong 82$  kcal which are in good agreement with values of 78 and 83 kcal, respectively, calculated from the heats of formation of the radicals. The heat of formation of the  $\text{C}_5\text{H}_{11}$  radical was estimated on the basis that  $D((\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)-\text{H}) = D((\text{CH}_3)_2\text{CH}-\text{H}) = 94.5$  kcal.

Benson and DeMore (27) have noted that problems may arise with the competitive shock-tube method, owing to fall-off in the rate constants at higher temperatures, if the two reactions do not have the same fall-off characteristics. With a proper choice of systems, however, the method shows considerable promise in determining bond dissociation energies.

## D. ESTIMATED ERRORS

The statistical errors in determining activation energies, arising from the limitations of the experimental measurements, are quite small. For metathetical reactions of the type previously described they usually fall within the range  $\pm 0.1$  to  $\pm 0.5$  kcal, while for pyrolytic reactions they are somewhat larger, about  $\pm 0.5$  to  $\pm 1$  kcal. Unfortunately, these are not the only source of errors to be considered, as all kinetic determinations of bond dissociation energies are dependent upon assumed values of some other activation energy or energies. Thus pyrolytic determinations rely upon an assumed value of  $E = 0$  for the reverse radical combination reaction, and, while this is a very reasonable assumption, it is possible that in certain cases a small reverse activation energy exists. Likewise for determinations based on metathetical reactions, it is frequently assumed that reactions such as



or



have zero activation energies, which may not be exactly true. Errors from assumed activation energies cannot be calculated. The over-all effect of these sources of errors is that bond strengths determined from metathetical reactions are usually accurate to  $\pm 1$  kcal and at least to  $\pm 2$  kcal while those from pyrolytic reactions are probably good to  $\pm 2$  kcal and occasionally

TABLE I  
 ACTIVATION ENERGIES<sup>a</sup> FOR REACTIONS X + RH = XH + R

R	X = I	Ref	X = Br	Ref	X = CH <sub>3</sub>	Ref	X = NF <sub>2</sub>	Ref	D(R-H) <sup>a</sup>
CH <sub>3</sub>	34.1	72, 80	18.3	60	14.5	100	...	...	104.0
C <sub>2</sub> H <sub>5</sub>	27.9	91	13.4	60	11.9	100	...	...	98.0
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	25.0	144	10.2	60	10.3	100	...	...	94.5
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	...	...	10.2	60	9.7	100	21.2	85	94.6
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	21.4	189	7.5	60	8.2	100	17.5	85	91.0
neo-C <sub>5</sub> H <sub>11</sub>	...	...	14.3	60	...	...	26.7	85	99.3
<i>c</i> -C <sub>5</sub> H <sub>11</sub>	...	...	...	...	9.1	73	19.9	85	92.9

<sup>a</sup> Units: kcal.

$\pm 1$  kcal. Benson (23), on the other hand, has stated that the pyrolytic method yields bond dissociation energies with errors of  $\pm 4$  kcal or greater. This seems an unrealistic estimate. It has already been pointed out (169), and this applies even more so now, that the self-consistency of the pyrolytic data and consistency with independent results confirm the general reliability of the method. The case of  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$  or  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  illustrates the point. The pyrolysis of ethylbenzene yields  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 43.2$  kcal while the pyrolysis of *n*-propylbenzene gives 44.5 kcal. The value recommended here from a variety of determinations is  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45 \pm 1$  kcal. It is highly unlikely that such good agreement would be obtained if the pyrolytic determinations involved errors of  $\pm 4$  kcal.

The errors in bond strengths calculated from heats of formation of radicals are a special case. The heats of formation of the hydrocarbon radicals are as accurately known as the bond strengths upon which they are based, since the heats of formation of the hydrocarbon molecules are known with high precision. This is not always so for other radicals. Calculated values for bonds formed between atoms and radicals have smaller errors than those formed between two radicals since the heats of formation of atoms are well established, but both types contain any errors associated with the heats of formation of the compounds. The errors in the heats of formation of nitrogen, sulfur, and halogen compounds can be considerable. In consequence the errors to be attached to calculated bond dissociation energies are sometimes as high as  $\pm 6$  kcal, but it should be remembered that for a series of related compounds the differences in bond dissociation energies will be known with more certainty than the actual values themselves, since some of the errors are canceled.

#### IV. POLANYI RELATIONS

By considering the shapes of the potential energy curves for the reactions of sodium atoms with alkyl halides, Evans and Polanyi (58) deduced, for a series of related reactions, that

$$E = \alpha\Delta H + C \quad (\text{Eq 20})$$

where  $E$  is the activation energy,  $\Delta H$  is the enthalpy change, and  $\alpha$  and  $C$  are constants. The implications

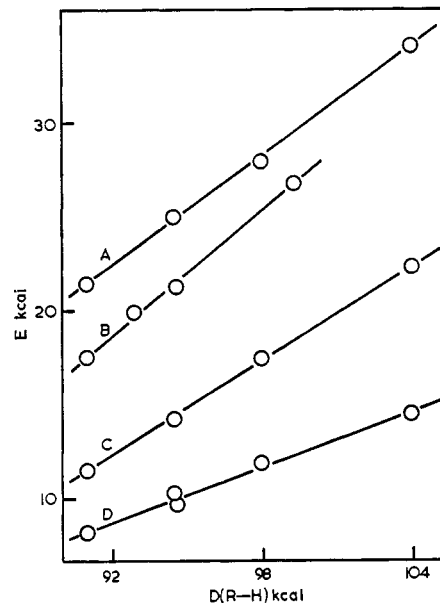
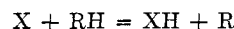


Figure 1.—Polanyi plots of  $E$  vs.  $D(\text{R-H})$  for reactions  $\text{X} + \text{RH} = \text{XH} + \text{R}$ : A, iodine atoms; B, difluoroamino radicals; C, bromine atoms ( $E$  displaced by +4 kcal); D, methyl radicals.

of this equation, usually referred to as the Polanyi relation, have been considered in detail by Trotman-Dickenson (191), but until recently attempts to verify it have failed owing to the lack of (i) accurate kinetic data and (ii) reliable bond dissociation energies. It has been shown that there is now sufficient information available on the reactions of methyl radicals with alkanes for a proper test to be made (192). Similar tests have also been made for the reactions of bromine atoms (61, 62) and difluoroamino radicals (85) with alkanes, and it is possible to apply the data for iodine atoms as well. For each of the reactions in the series



( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, t\text{-C}_4\text{H}_9$ , etc.) the same bond is being formed irrespective of the change in the alkyl radical, so that  $\Delta H$  can be represented by the strength of the bond which is being broken, *i.e.*,  $D(\text{R-H})$ . Equation 20 then takes the form

$$E = \alpha(D(\text{R-H}) - C_1)$$

and  $E$  is plotted against  $D(\text{R-H})$  for each series of reactions as in Figure 1. The relevant data are summarized in Table I.



The activation energies for the reactions of difluoroamino radicals with *n*- and isobutane have been corrected from the original values (85) to allow for attack on the primary C-H bonds in these molecules. The bond dissociation energies listed in the final column of Table I are the values recommended in this review and discussed in subsequent sections.

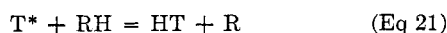
The constants,  $\alpha$  and  $C_1$ , in the Polanyi relations have been calculated from the plots and are listed in Table II.

TABLE II  
POLANYI CONSTANTS FOR HYDROGEN ABSTRACTION  
FROM ALKANES

Radical or atom	$\alpha$	$C_1$
I	0.97	69.0
NF <sub>2</sub>	1.1	76.1
Br	0.86	82.5
CH <sub>3</sub>	0.49	74.3

The excellent linear plots confirm the Polanyi relation and strongly support the amended values of the bond dissociation energies of the alkanes. It must be emphasized, however, that this type of relation is only applicable to reactions of radicals or atoms with a series of closely related compounds. It has been stressed (27), by taking the example of the reactions of methyl radicals with a variety of substrates, that there is no way of relating the activation energies and enthalpy changes when the substrates are different classes of compounds.

An interesting correlation of the same general type as the Polanyi relation has been noted (33, 163) for the reactions of recoil tritium atoms (T\*) with alkanes



The yields of HT from reaction 21 for a series of alkanes (methane to neopentane) were measured under carefully controlled and standardized conditions and taken as a measure of the extent of reaction 21. These HT yields were then expressed per C-H bond in the molecule and relative to an HT yield of 0.79 from methane. When the resulting relative HT yields are plotted against the appropriate bond dissociation energies in the alkanes, there is an approximate linear relation. This probably confirms the general correctness of the procedure, but the precision of the Polanyi plots, for say bromine or iodine atom reactions, is lacking. Until more accurate data can be obtained on the recoil tritium reactions it is doubtful if the method will yield more than approximate bond dissociation energies.

## V. VALUES OF BOND DISSOCIATION ENERGIES

This section contains the bulk of the review and deals with the experimental results on bond dissociation energies by kinetic methods. Bond dissociation energies calculated from heats of formation of radicals, listed

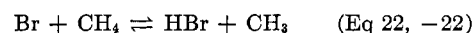
in Table XXX, are also included where these are the best available values. The selection of calculated bond dissociation energies is somewhat arbitrary but is mainly based on current interest.

### A. HYDROCARBONS

#### 1. Alkanes

##### a. $D(\text{CH}_3\text{-H})$

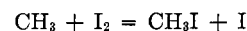
Until 1961 the accepted value of  $D_{298}(\text{CH}_3\text{-H})$  was 102.5 kcal, mainly supported by work (118) on the bromination of methane



Thus

$$D(\text{CH}_3\text{-H}) = D(\text{H-Br}) + E_{22} - E_{-22}$$

Kistiakowsky and Van Artsdalen determined  $E_{22}$  to be 17.8 kcal and from an assumed value of  $E_{-22}$  they deduced  $D(\text{CH}_3\text{-H}) = 102$  kcal. Fetti and Trotman-Dickenson (61) subsequently determined  $E_{-22}$  experimentally, by treating methyl radicals with mixtures of HBr and I<sub>2</sub> and by making the reasonable assumption of zero activation energy for reaction -10



Hence  $E_{-22}$  was found to be 1.4 kcal, which is 0.7 kcal less than the value formerly assumed (118). At the same time (60) reaction 22 was reinvestigated by the competitive bromination technique described in section IIIB2, and  $E_{22}$  determined to be 18.3 kcal, which it was argued was in good agreement with the previous result (17.8 kcal) since Kistiakowsky and Van Artsdalen had calculated a "collision theory" activation energy, as opposed to the more conventional Arrhenius activation energy.

From the revised determinations of  $E_{22}$  and  $E_{-22}$ , it was deduced (61) that

$$D_{460}(\text{CH}_3\text{-H}) = D_{460}(\text{H-Br}) + 16.9 = 104.8 \text{ kcal}$$

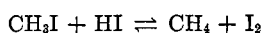
at the mean experimental temperature of 460°K, and hence

$$D_{298}(\text{CH}_3\text{-H}) = 103.9 \text{ kcal}$$

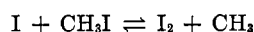
It should also be noted that part of the difference between the amended value of  $D(\text{CH}_3\text{-H})$  and the original value of Kistiakowsky and Van Artsdalen (118) arises from a revised value of  $D(\text{H-Br})$ . The revised value of  $D(\text{CH}_3\text{-H})$  has been criticized (48) on the grounds that  $E_{22}$  should be corrected to allow for a negative activation energy of -2 kcal for the recombination of bromine atoms, which would have the effect of lowering  $D(\text{CH}_3\text{-H})$  to 103 kcal. While there is evidence for such a negative activation energy, the actual value may not be as low as -2 kcal. The value of  $D(\text{CH}_3\text{-H}) = 103.9$  kcal is to be preferred with allowance in the es-

timated errors for the possibility of a negative activation energy for bromine atom recombination.

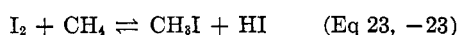
Further direct evidence confirming the revised higher value of  $D(\text{CH}_3\text{-H})$  has been obtained from kinetic studies of the reactions of HI with  $\text{CH}_3\text{I}$  (64) and of  $\text{I}_2$  with  $\text{CH}_4$  (72, 80). The kinetic results on the system



lead to accurate determinations of the Arrhenius parameters for reaction 10, -10



The method was outlined in section IIIB1. The rate constants,  $k_{10}$ , determined by this method are supported by less extensive results (72, 80) on the system



$E_{10}$  was shown to be 20.5 kcal at 560°K and corrected (72) to 20.2 kcal at 298°K, and if  $E_{-10}$  is assumed to be zero this yields

$$\Delta H_{10,-10} = 20.2 \text{ kcal}$$

$\Delta H_f^\circ(\text{CH}_3)$  follows from

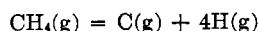
$$\Delta H_{10,-10}^\circ = \Delta H_f^\circ(\text{CH}_3) + \Delta H_f^\circ(\text{I}_2(\text{g})) - \Delta H_f^\circ(\text{I}) - \Delta H_f^\circ(\text{CH}_3\text{I}) \quad (\text{Eq 24})$$

Since the heat of formation of the iodine atom is known accurately from spectroscopic data, this leaves  $\Delta H_f^\circ(\text{CH}_3\text{I})$  as the largest uncertainty in Eq 24. Two independent studies (72, 80) of the equilibrium reactions, 23 and -23, have recently confirmed the value  $\Delta H_f^\circ(\text{CH}_3\text{I}) = 3.28 \pm 0.16$  kcal. Thus from Eq 24,  $\Delta H_f^\circ(\text{CH}_3)$  becomes 34.1 kcal, and it follows that  $D(\text{CH}_3\text{-H}) = 104.1$  kcal. The errors in both these quantities have been quoted (72) as  $\pm 0.5$  kcal. A value of  $E_{10} = 19.2$  kcal has also been reported from a study of reaction 10 in a flow system with HI as the carrier gas (31). As this appears to be a preliminary publication in which experimental details are lacking, it seems advisable to accept the figure of  $E_{10} = 20.2$  kcal determined by Flowers and Benson (64).

In addition to this convincing direct evidence for  $D(\text{CH}_3\text{-H})$  close to 104 kcal, there is also the indirect evidence of the Polanyi relations described in section IV. The value  $D(\text{CH}_3\text{-H}) = 104.0$  kcal will be adopted here. The maximum errors are  $\pm 1$  kcal.

#### b. $D(\text{CH}_2\text{-H})$ and $D(\text{CH-H})$

The sum of  $D(\text{CH}_2\text{-H})$  and  $D(\text{CH-H})$  can be determined from thermochemistry and a knowledge of  $D(\text{C-H})$  and  $D(\text{CH}_3\text{-H})$ . The heat of the reaction



can be calculated from enthalpy data at 298°K, to be  $\Delta H_{298} = 397$  kcal, and it follows that

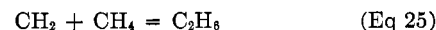
$$D(\text{CH}_3\text{-H}) + D(\text{CH}_2\text{-H}) + D(\text{CH-H}) + D(\text{C-H}) = 397 \text{ kcal}$$

Taking  $D(\text{CH}_3\text{-H}) = 104$  and  $D(\text{C-H}) = 81$  kcal this gives

$$(D(\text{CH}_2\text{-H}) - D(\text{CH-H})) = 212 \text{ kcal}$$

A determination of either  $D(\text{CH}_2\text{-H})$  or  $D(\text{CH-H})$  will therefore suffice to fix both quantities.

$D(\text{CH}_2\text{-H})$  has been determined (19) from the activation energy of the reaction



$E_{25}$  was deduced to be 88 kcal by applying unimolecular rate theory to comparison of the lifetime of the excited  $\text{C}_2\text{H}_6$  from reaction 25, with the lifetime of the ethane produced by the association of two methyl radicals. From the thermodynamic cycle

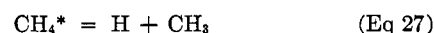
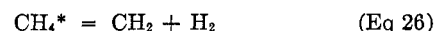
	$\Delta H$
$\text{CH}_4 = \text{CH}_3 + \text{H}$	104
$\text{CH}_2 + \text{H} = \text{CH}_3$	$-D(\text{CH}_2\text{-H})$
$\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$	-88
$\text{CH}_2 + \text{CH}_4 = \text{C}_2\text{H}_6$	-88

it follows that  $D(\text{CH}_2\text{-H}) = 104$  kcal.

Support for this determination was also obtained in the same study (19) from the reaction of methylene with hydrogen. The excited methane resulting from the reaction



can decompose in two ways



and since they could only find evidence for reaction 27, Bell and Kistiakowsky (19) made the simple assumption that  $E_{26} \geq E_{27}$ . From  $D(\text{CH}_3\text{-H}) = 104$  kcal it follows that  $E_{26} \geq 104$  kcal, and from the cycle of reactions

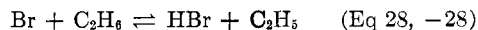
	$\Delta H$
$\text{CH}_4 = \text{CH}_2 + \text{H}_2$	$\geq 104$
$\text{CH}_3 + \text{H} = \text{CH}_4$	-104
$\text{H}_2 = 2\text{H}$	104
$\text{CH}_2 = \text{CH}_2 + \text{H}$	$D(\text{CH}_2\text{-H})$

we have  $D(\text{CH}_2\text{-H}) \geq 104$  kcal.

On the basis of  $D(\text{CH}_2\text{-H}) = 104$  kcal and the sum ( $D(\text{CH}_2\text{-H}) + D(\text{CH-H}) = 212$  kcal,  $D(\text{CH-H})$  becomes 108 kcal. It must be emphasized that while these kinetic values are in substantial agreement with recent spectroscopic results (93), they are subject to fairly large errors. Bell and Kistiakowsky (19) suggest  $\pm 6$  kcal. Nevertheless they form a useful basis for discussion and are the only means of obtaining a kinetic estimate of the heat of formation of the  $\text{CH}_2$  radical.

#### c. $D(\text{C}_2\text{H}_5\text{-H})$

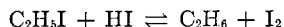
A revised figure for  $D(\text{C}_2\text{H}_5\text{-H})$  has been confirmed by studies analogous to those for  $D(\text{CH}_3\text{-H})$ . The bromination of ethane and the reverse reaction have been



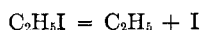
studied by Fettis, Knox, and Trotman-Dickenson (60) and by Fettis and Trotman-Dickenson (61), respectively. The method was described in section IIIB2 and gave

$$D_{298}(\text{C}_2\text{H}_5\text{-H}) = 98.2 \text{ kcal}$$

The reaction



has been studied (91) by a method similar to that for the HI-CH<sub>3</sub>I system (64), and leads to  $D(\text{C}_2\text{H}_5\text{-I}) = 52.9$  kcal. Thus for the reaction



we have

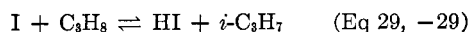
$$D(\text{C}_2\text{H}_5\text{-I}) = \Delta H_f^\circ(\text{C}_2\text{H}_6) + \Delta H_f^\circ(\text{I}) - \Delta H_f^\circ(\text{C}_2\text{H}_5\text{I})$$

and taking  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{I}) = -2.1$  kcal (9) this gives  $\Delta H_f^\circ(\text{C}_2\text{H}_6) = 25.3$  kcal corresponding to  $D(\text{C}_2\text{H}_5\text{-H}) = 97.7$  kcal.

Trotman-Dickenson (192) has suggested a weighted mean value of  $D(\text{C}_2\text{H}_5\text{-H}) = 98.0$  kcal with errors of  $\pm 1$  kcal, and this is supported by the Polanyi relations described in section IV.

#### d. $D((\text{CH}_3)_2\text{CH-H})$

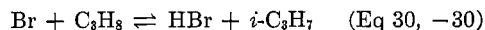
The most direct evidence on this bond dissociation energy comes from results on the reaction between iodine and propane (144). By a kinetic treatment similar to that employed in the RI-HI systems accurate rate data was obtained for the reaction



resulting in the value  $E_{29} = 25.0$  kcal. Reaction -29 has not been studied but, by assuming  $E_{-29} = 1$  kcal,  $D(i\text{-C}_3\text{H}_7\text{-H})$  was calculated (144) to be 94.5 kcal from the equation

$$D(\text{C}_3\text{H}_7\text{-H}) = D(\text{H-I}) + E_{29} - E_{-29}$$

This value had been precisely predicted (61) from the results on the bromination of propane



where  $E_{30}$  was shown to be 10.2 kcal. Although  $E_{-30}$  was not measured the value  $D(i\text{-C}_3\text{H}_7\text{-H}) = 94.5$  kcal was calculated from the Polanyi equation for the reactions of bromine with alkanes

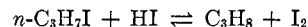
$$E_{\text{Br}} = 0.86[D(\text{C-H}) - 82.5]$$

The value  $D(i\text{-C}_3\text{H}_7\text{-H}) = 94.5 \pm 1$  kcal is adopted here.

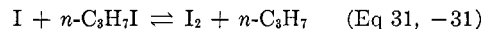
#### e. $D(\text{CH}_3\text{CH}_2\text{CH}_2\text{-H})$

This bond should be of similar strength to  $D(\text{C}_2\text{H}_5\text{-H})$ , *i.e.*, about 98 kcal. Direct bromination or reaction with iodine is not feasible since there is preferential attack at the secondary C-H bonds.

A value of the heat formation of the *n*-propyl radical can be deduced from the kinetics of the reaction



The original results (145) have been reinterpreted (28, 176) on the basis of the free-radical mechanism which is now generally accepted for this type of system. The activation energy for the reaction



was calculated to be  $E_{31} = 18$  kcal, and, if  $E_{-31}$  is assumed to be zero, this yields  $D(n\text{-C}_3\text{H}_7\text{-I}) = 54$  kcal. Hence from  $\Delta H_f^\circ(n\text{-C}_3\text{H}_7\text{I}) = -7.1$  kcal (24),  $\Delta H_f^\circ(\text{C}_3\text{H}_7)$  is deduced to be 21.4 and  $D(n\text{-C}_3\text{H}_7\text{-H})$  is 98.3 kcal. Unfortunately, the kinetic data upon which  $E_{31}$  is based are not of the same precision as those for the other RI-HI systems reinvestigated by Benson and his group. At the same time the heat of formation of *n*-propyl iodide is not as well known as that of methyl or ethyl iodide, and accordingly the deduced value of  $D(n\text{-C}_3\text{H}_7\text{-H})$  has probable errors of about  $\pm 2$  kcal.

An experimental value of  $\Delta H_f^\circ(n\text{-C}_3\text{H}_7)$  has been obtained from the pyrolysis of *n*-butylbenzene, studied by the aniline-carrier technique (55).



The rate constant for this reaction is given by

$$\log k_{32} = 14.5 - (67.2/\theta)$$

and hence  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-C}_3\text{H}_7) = 67.2$  kcal. From the heat of formation of the benzyl radical, 45 kcal (see section VA2), and of *n*-butylbenzene (-3.3 kcal (165)) it can be shown that  $\Delta H_f^\circ(n\text{-C}_3\text{H}_7) = 18.9$  and  $D(n\text{-C}_3\text{H}_7\text{-H}) = 96$  kcal. Both results, so far discussed, lie within the limits  $D(n\text{-C}_3\text{H}_7\text{-H}) = 98 \pm 2$  kcal.

Even better agreement with this figure is obtained from the results on the decomposition of the *n*-propyl radical, but this is probably largely fortuitous since radical decompositions are among the most difficult reactions to study. The reaction



has been extensively investigated in recent years (40, 99, 106, 110). Kerr and Calvert (106) have summarized the previous results and deduced  $E_{33} = 34.5$  kcal by studying the decomposition reaction of the radicals produced from the photolysis of azo-*n*-propane. In conjunction with  $E_{-33} = 8.6$  kcal for the addition of methyl radicals to ethylene (34) this yields  $D(\text{CH}_3\text{-CH}_2\text{CH}_2) = 25.9$  kcal and hence from the equation

$$D(\text{CH}_3\text{-CH}_2\text{CH}_2) =$$

$$\Delta H_f^\circ(\text{CH}_3) + \Delta H_f^\circ(\text{C}_2\text{H}_4) - \Delta H_f^\circ(n\text{-C}_3\text{H}_7)$$

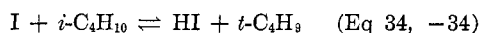
$\Delta H_f^\circ(n\text{-C}_3\text{H}_7)$  is deduced to be 20.4 kcal and  $D(n\text{-C}_3\text{H}_7\text{-H}) = 97.3$  kcal.

Further evidence in support of a value  $D(n\text{-C}_3\text{H}_7\text{-H}) \cong D(\text{C}_2\text{H}_5\text{-H})$  can be taken from the fact that the activation energies for the reactions of methyl radicals with ethane and the primary C-H in propane are equal within the experimental errors (100). Results presented later in this review show that the primary C-H bond dissociation energy in neopentane is significantly higher than  $D(\text{C}_2\text{H}_5\text{-H})$ , so it seems extremely unlikely that  $D(n\text{-C}_3\text{H}_7\text{-H})$  should be less than  $D(\text{C}_2\text{H}_5\text{-H})$ . The value  $D(n\text{-C}_3\text{H}_7\text{-H}) = 98 \pm 2$  kcal is recommended.

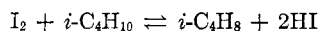
f.  $D((\text{CH}_3)_3\text{C-H})$

The situation for this bond dissociation energy is identical with that for  $D(i\text{-C}_3\text{H}_7\text{-H})$ . Experiments on the reaction of iodine atoms with isobutane have confirmed the earlier prediction from the bromination study and the Polanyi relation.

Teranishi and Benson (189) found  $E_{34} = 21.4$  kcal for the reaction



from a kinetic study of the over-all reaction



The rate of disappearance of  $\text{I}_2$  was measured with a spectrophotometer. Thus assuming  $E_{-34} = 1.4$  kcal, they deduced  $D(t\text{-C}_4\text{H}_9\text{-H}) = 90.9$  kcal. A value of 91.4 kcal had previously been obtained (61) from an experimental activation energy,  $E_{35} = 7.5$  kcal, for the reaction



and the Polanyi equation.

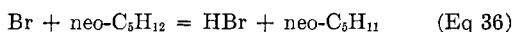
The weighted mean value (192) of  $D(t\text{-C}_4\text{H}_9\text{-H}) = 91.0 \pm 1$  kcal is adopted here.

g.  $D(\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{-H})$

There is no direct experimental determination of this bond strength but  $D(\text{sec-C}_4\text{H}_9\text{-H}) = 94.6$  kcal has been deduced (61) from bromination studies and the Polanyi rule. Since the values predicted by the same procedure for  $D(i\text{-C}_3\text{H}_7\text{-H})$  and  $D(t\text{-C}_4\text{H}_9\text{-H})$  have subsequently been confirmed, there is every reason for accepting  $D(\text{sec-C}_4\text{H}_9\text{-H}) = 94.6 \pm 1$  kcal.

h.  $D((\text{CH}_3)_3\text{CCH}_2\text{-H})$

Here again the best available value is that deduced from  $E_{36} = 14.3$  kcal for the reaction



and the Polanyi equation (61). It is interesting to note that the value obtained,  $D(\text{neo-C}_5\text{H}_{11}\text{-H}) = 99.3 \pm 1$  kcal is significantly higher than  $D(\text{C}_2\text{H}_5\text{-H})$ .

i.  $D(\text{C-C})$  in Alkanes

The best available values of these bond dissociation energies are obtained from the equation

$$D(\text{R-R}_1) = \Delta H_f^\circ(\text{R}) + \Delta H_f^\circ(\text{R}_1) - \Delta H_f^\circ(\text{RR}_1)$$

The following results were calculated from the heats of formation of the alkyl radicals listed in Table XXX. Many more values can be derived in the same way. The estimated errors are  $\pm 2$  kcal.

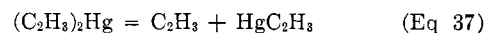
TABLE III  
CALCULATED  $D(\text{C-C})$  VALUES IN ALKANES

Bond	$D$ , kcal	Bond	$D$ , kcal
$\text{CH}_3\text{-CH}_3$	88	$\text{C}_2\text{H}_5\text{-C}_2\text{H}_5$	87
$\text{CH}_3\text{-C}_2\text{H}_5$	85	$\text{C}_2\text{H}_5\text{-CH}(\text{CH}_3)_2$	80
$\text{CH}_3\text{-CH}(\text{CH}_3)_2$	83	$(\text{CH}_3)_2\text{CH-CH}(\text{CH}_3)_2$	78

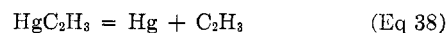
2. Alkenes

a.  $D(\text{CH}_2=\text{CH-H})$

A value of  $D(\text{C}_2\text{H}_3\text{-H})$  has been deduced from the pyrolysis of divinylmercury by the toluene-carrier technique (194). The initial decomposition reaction



is followed by



so that the reaction could be studied by the rate of formation of mercury as well as by the rate of formation of gaseous products. Reaction 37 was shown to be homogeneous and unimolecular with a rate constant of

$$\log k_{37} = 11.9 - (48.3/\theta)$$

and hence  $D(\text{C}_2\text{H}_3\text{-HgC}_2\text{H}_3)$  was taken to be 48.3 kcal.  $D(\text{C}_2\text{H}_3\text{-H})$  was then obtained from the relation

$$D(\text{CH}_3\text{-HgCH}_3) - D(\text{C}_2\text{H}_3\text{-HgC}_2\text{H}_3) = 2D(\text{CH}_3\text{-H}) - 2D(\text{C}_2\text{H}_3\text{-H})$$

on the assumption that there is no interaction between the two double bonds in divinylmercury and that the activation energy for reaction 38 is the same as that for the analogous reaction in the decomposition of dimethylmercury. Substituting the values  $D(\text{CH}_3\text{-Hg-CH}_3) = 51.3$  kcal (153) and  $D(\text{CH}_3\text{-H}) = 104.0$  kcal yields  $D(\text{C}_2\text{H}_3\text{-H}) = 102.5$  kcal, but, as the authors note, the uncertainty in this determination is considerable and minimum errors of  $\pm 3$  kcal have been assigned.

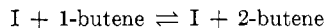
Harrison and Lossing (90) have reported  $D(\text{C}_2\text{H}_3\text{-H}) = 105 \pm 3$  kcal, from electron impact measurements, so there is reasonable agreement and the value  $D(\text{C}_2\text{H}_3\text{-H}) = 104 \pm 2$  kcal would seem to be compatible with both determinations.

b.  $D(\text{CH}_2=\text{CHCH}_2\text{-H})$

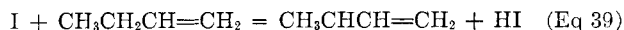
There is no direct experimental determination in this case, but a value can be derived from either the resonance energy or the heat of formation of the allyl radical.

The resonance energy of the allyl radical is defined

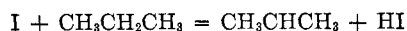
as the difference between the bond dissociation energies  $D(\text{CH}_3\text{CH}_2\text{CH}_2\text{-H})$  and  $D(\text{CH}_2=\text{CHCH}_2\text{-H})$  and has been determined from a study of the iodine-catalyzed isomerization of 1-butene (54). The over-all reaction is



and by a steady-state treatment of the detailed mechanism it has been possible to obtain an activation energy for the step



corresponding to  $E_{39} = 12.4$  kcal. Previously the value  $E_{29} = 25.0$  kcal had been reported (144) for reaction 29

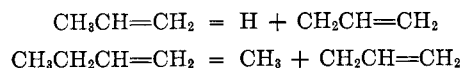


which was identified with the activation energy for the analogous reaction with *n*-butane, since  $D(i\text{-C}_3\text{H}_7\text{-H}) \cong D(\text{sec-C}_4\text{H}_9\text{-H})$ . It follows that the resonance energy of the methallyl radical is given by  $E_{29} - E_{39} = 12.6$  kcal, and this can be taken as the resonance energy of the allyl radical itself. From the definition of the resonance energy we have

$$D(\text{CH}_2=\text{CHCH}_2\text{-H}) = D(n\text{-C}_3\text{H}_7\text{-H}) - 12.6 \cong 85 \text{ kcal}$$

The above value of the resonance energy of the allyl radical has been confirmed by subsequent results of Egger and Benson (53).

In principle the heat of formation of the allyl radical should be obtainable from the pyrolyses of propylene or 1-butene

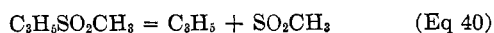


The pyrolysis of propylene is extremely complex, however, and yields no reliable information on  $D(\text{C}_3\text{H}_5\text{-H})$ . Early results (168, 182) on the pyrolysis of 1-butene led to a much lower value of  $D(\text{CH}_2=\text{CHCH}_2\text{-H})$  than that described above. This difficulty has recently been resolved by a reinvestigation of the pyrolysis of 1-butene by the aniline-carrier technique (109), where it was shown that the first-order rate constants were measured in the pressure-sensitive region, and hence the experimental activation energy was considerably less than the limiting pressure value.

Results on the decomposition of allyl methyl sulfone by the toluene-carrier technique can also be used to obtain  $\Delta H_f^\circ(\text{C}_3\text{H}_5)$ . Busfield and Ivin (36) have determined

$$\log k_{40} = 14.1 - (47.7/\theta)$$

for the pyrolysis reaction



and thus

$$\begin{aligned} \Delta H_f^\circ(\text{C}_3\text{H}_5) &= D(\text{C}_3\text{H}_5\text{-SO}_2\text{CH}_3) - \\ &\quad \Delta H_f^\circ(\text{SO}_2\text{CH}_3) + \Delta H_f^\circ(\text{C}_3\text{H}_5\text{SO}_2\text{CH}_3) \end{aligned}$$

$\Delta H_f^\circ(\text{C}_3\text{H}_5\text{SO}_2\text{CH}_3)$  has been shown to be  $-73.5$  kcal (37) and  $\Delta H_f^\circ(\text{SO}_2\text{CH}_3)$  can be calculated as  $-63.2$  kcal (see section VD2), so that  $\Delta H_f^\circ(\text{C}_3\text{H}_5)$  is 37.4 kcal, corresponding to  $D(\text{C}_3\text{H}_5\text{-H}) = 84.6$  kcal, in excellent agreement with the value deduced from the resonance energy approach.

Similarly a value can be calculated from the pyrolysis of allyl bromide, investigated by the toluene-carrier technique (181, 190) and found to have an activation energy of  $E_{41} = 47.5$  kcal, presumed to correspond to the reaction



Hence from  $\Delta H_f^\circ(\text{C}_3\text{H}_5\text{Br}) = 12.1$  kcal (162) it can be deduced that  $\Delta H_f^\circ(\text{C}_3\text{H}_5) = 32.9$  kcal, which is obviously a considerable underestimate. Although the heat of formation of allyl bromide may not be known with high precision, the most likely source of error is in the pyrolysis data, probably arising from an oversimplified mechanism.

In spite of the results from the pyrolysis of allyl bromide, the value  $D(\text{C}_3\text{H}_5\text{-H}) = 85 \pm 1$  kcal would seem reasonably well established.

### 3. Cycloalkanes

Bond strengths in cycloalkanes have been deduced (192) from the activation energies ( $E_{Me}$ ) for methyl attack on the cycloalkanes and the Polanyi relation for methyl radicals and alkanes

$$E_{Me} = 0.49[D(\text{C-H}) - 74.3] \quad (\text{Eq 42})$$

The results are summarized in Table IV.

TABLE IV  
REACTIONS OF METHYL RADICALS WITH CYCLOALKANES

Compound	$E_{Me}$ , kcal	Ref	$D(\text{C-H})$ , kcal
Cyclopropane	13.1	73	101
Cyclobutane	10.3	74	95
Cyclopentane	9.3	73	93
Cyclohexane	9.7	73	94
Cycloheptane	9.1	73	93

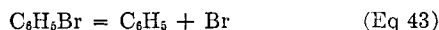
It must not be overlooked, however, that these activation energies may be affected by the strain energies in the cycloalkanes and their activated complexes with methyl radicals (74, 192). The above bond dissociation energies are, therefore, only tentative with minimum errors of  $\pm 3$  kcal.

### 4. Aromatic Hydrocarbons

#### a. $D(\text{C}_6\text{H}_5\text{-H})$

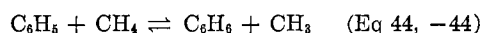
The kinetic results bearing on  $D(\text{C}_6\text{H}_5\text{-H})$  are somewhat conflicting. An early study (186) of the pyroly-

sis of phenyl bromide leads to a value of  $\Delta H_f^\circ(\text{C}_6\text{H}_5) = 69.6$  kcal from  $E_{43} = 70.9$  kcal for the reaction



in conjunction with  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{Br}) = 25.4$  kcal (186). Hence  $D(\text{C}_6\text{H}_5\text{-H})$  is given by 101.9 kcal. This determination has been criticized (63) because of the high temperatures employed in the pyrolysis and the uncertainty in the heat of formation of phenyl bromide. Certainly, minimum errors of  $\pm 3$  kcal should be attached to it.

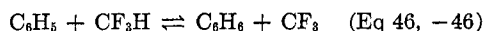
Two investigations, leading to  $D(\text{C}_6\text{H}_5\text{-H})$  by the metathetical approach, were carried out almost simultaneously. Duncan and Trotman-Dickenson (52) produced phenyl radicals by photolyzing acetophenone and studied the reactions



by analyzing for the benzene and biphenyl.  $E_{44}$  was found to be 11.1 kcal, relative to an assumed value of  $E_{45} = 0$ . In conjunction with  $E_{-44} = 9.2$  kcal (193), deduced from the photolysis of acetone in the presence of benzene, this gives

$$D(\text{C}_6\text{H}_5\text{-H}) = D(\text{CH}_3\text{-H}) - E_{44} + E_{-44} = 102.1 \text{ kcal}$$

Fielding and Pritchard (63) studied reaction 44, by generating the phenyl radicals from the photolysis of diphenylmercury, and determined  $E_{44} = 7.5$  kcal leading to  $D(\text{C}_6\text{H}_5\text{-H}) = 105.7$  kcal, on the basis of  $D(\text{CH}_3\text{-H}) = 104.0$  kcal. Further evidence for a higher value was obtained by the same workers from a study of the reactions



for which the following relation applies

$$D(\text{C}_6\text{H}_5\text{-H}) = D(\text{CF}_3\text{-H}) - E_{46} + E_{-46}$$

$E_{46}$  was shown to be 5.2 kcal and taking  $E_{-46} = 6.3$  kcal (43), this gives  $D(\text{C}_6\text{H}_5\text{-H}) = 107$  from  $D(\text{CF}_3\text{-H}) = 106$  kcal (see section VE1). This value is higher than that calculated by the original authors owing to the amended value of  $D(\text{CF}_3\text{-H})$ .

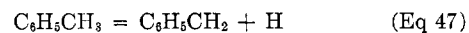
Obviously there is a considerable discrepancy between the two estimates of  $E_{44}$ , leading to different values of  $D(\text{C}_6\text{H}_5\text{-H})$ , and until this is resolved the correct value of  $D(\text{C}_6\text{H}_5\text{-H})$  will be in doubt. In the meantime the value  $D(\text{C}_6\text{H}_5\text{-H}) = 104 \pm 2$  kcal is recommended.

#### b. $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$

In recent years  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$  has been one of the most controversial values in the literature, but the situation now seems reasonably clear.

The most recent kinetic results on the pyrolysis of toluene itself, studied under carefully controlled con-

ditions, have been reported by Price (151) who obtained for the reaction



$$\log k_{47} = 14.8 - (85.0/\theta)$$

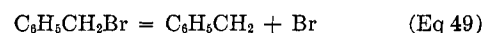
Hence from  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 85.0$  kcal,  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{-CH}_2) = 44.9$  kcal.

$E_{45} = 7.2$  kcal has been determined (5) for the bromination of toluene and  $E_{-45} = 5.0$  kcal for the

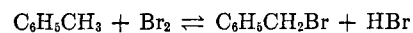


reverse reaction, from a study of the hydrogen bromide inhibited reaction (5). This determination of  $E_{-45}$  was based on an assumed value of zero activation energy for the reaction of benzyl radicals with molecular bromine. It has been argued (55) that the activation energy of the latter reaction is probably nearer 5 kcal, by analogy with the reaction of trichloromethyl radicals with bromine (177). The amended value of  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$  was thus calculated to be 84.5 kcal (55).

The other determinations of  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$  depend upon measurement of  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$ . The activation energy for the pyrolysis of benzyl bromide has

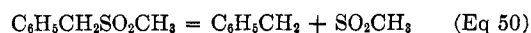


been confirmed to be  $E_{49} = 51$  kcal by several toluene-carrier investigations (125, 127, 181). Taking  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{Br}) = 20$  kcal, as determined (25) from a thermodynamic study of the equilibrium



this yields  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 44.3$  kcal and  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 84$  kcal.

A further value can be obtained from the toluene-carrier pyrolysis of benzyl methyl sulfone (36). The rate constant for the reaction

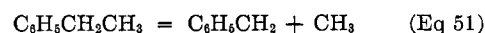


was shown to be

$$\log k_{50} = 14.5 - (51.3/\theta)$$

Thus, from  $\Delta H_f^\circ(\text{SO}_2\text{CH}_3) = -63.2$  kcal (see section VD2) and  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_3) = -68.0$  kcal (37),  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  is found to be 46.5 kcal, leading to  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 86.6$  kcal.

Even more convincing evidence in support of these values of  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  and  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$  has been put forward from a reinvestigation of the pyrolyses of ethyl- and *n*-propylbenzenes by the aniline-carrier method (55). For the decomposition reactions



it was shown that

$$\log k_{51} = 14.6 - (70.1/\theta)$$

TABLE V  
KINETIC RESULTS FOR  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  AND  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$

Reaction	Method	$\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$ , kcal	$D(\text{C}_6\text{H}_5\text{CH}_2\text{-H})$ kcal	Ref
$\text{C}_6\text{H}_5\text{CH}_3 = \text{C}_6\text{H}_5\text{CH}_2 + \text{H}$	Flow system	...	85	151
$\text{Br} + \text{C}_6\text{H}_5\text{CH}_2 = \text{HBr} + \text{C}_6\text{H}_5\text{CH}_2$	Metathetical	...	84.6	55
$\text{C}_6\text{H}_5\text{CH}_2\text{Br} = \text{C}_6\text{H}_5\text{CH}_2 + \text{Br}$	Toluene-carrier	44.3	...	25
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_3 = \text{C}_6\text{H}_5\text{CH}_2 + \text{SO}_2\text{CH}_3$	Toluene-carrier	46.5	...	36
$\text{C}_6\text{H}_5\text{C}_2\text{H}_5 = \text{C}_6\text{H}_5\text{CH}_2 + \text{CH}_3$	Aniline-carrier	43.2	...	55
$\text{C}_6\text{H}_5\text{C}_3\text{H}_7 = \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_2\text{H}_5$	Aniline-carrier	44.5	...	55

and

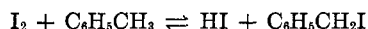
$$\log k_{52} = 14.9 - (68.6/\theta)$$

both considerably different from the values originally obtained by the toluene-carrier technique (178). Hence from  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-CH}_3) = 70.1$  and  $D(\text{C}_6\text{H}_5\text{-CH}_2\text{-C}_2\text{H}_5) = 68.6$  kcal it follows that  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{-CH}_2) = 43.2$  or  $44.5$  kcal.

The results so far discussed are summarized in Table V. These results clearly support values of  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 85$  and  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45$  kcal.

The situation became more complex, however, when the values  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{Br}) = 15.1$  and  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{I}) = 23.9$  kcal were reported (10) from the heats of hydrogenation of the halides with lithium aluminum hydride. These figures lead to values of  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 39.4$  and  $38.4$  kcal, respectively, from the activation energies of the decomposition of benzyl bromide (51 kcal) and benzyl iodide (40 kcal). The difficulty in deciding between the values  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45$  or  $40$  kcal has been emphasized by Skinner (170).

Fortunately the issue seems to have been resolved by a recent study of the equilibrium



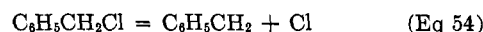
leading to  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{I}) = 30.4$  kcal (204). In conjunction with the pyrolysis data on benzyl iodide this gives  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45.1$  kcal. At the same time  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 44.1$  kcal was reported (204) from a kinetic study of the reaction



for which  $E_{53} = 14.4$  kcal was deduced.  $E_{-53}$  was assumed to be  $1.5$  kcal.

The conclusion must therefore be drawn that  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{I})$  obtained from the reduction experiments with lithium aluminum hydride (10) is seriously wrong. Similarly  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{Br})$  reported in the same paper must also be wrong, and the previous result of Benson and Buss (25) by the equilibrium method is to be preferred.

The values  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45 \pm 1$  and  $D(\text{C}_6\text{H}_5\text{-CH}_2\text{-H}) = 85 \pm 1$  kcal can now be accepted with confidence. One further check would be possible if the heat of formation of benzyl chloride were known, since the rate constant for the decomposition



has been determined (184) to be

$$\log k_{54} = 14.83 - (68.0/\theta)$$

c.  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-R})$

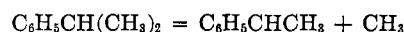
Bond dissociation energies in compounds where R =  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or  $n\text{-C}_3\text{H}_7$  have already been referred to in connection with either  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  or  $\Delta H_f^\circ(n\text{-C}_3\text{H}_7)$ . The three results, which are listed in Table VI, were obtained by aniline-carrier pyrolyses (55). Maximum errors are estimated as  $\pm 2$  kcal.

TABLE VI  
EXPERIMENTAL VALUES OF  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-R})$

R	$D(\text{C}_6\text{H}_5\text{CH}_2\text{-R})$ , kcal	Ref
$\text{CH}_3$	70	55
$\text{C}_2\text{H}_5$	69	55
$n\text{-C}_3\text{H}_7$	67	55

d.  $D(\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{-CH}_3)$

This is a good example of how aniline-carrier results have substantially corrected original toluene-carrier data. The decomposition reaction is (Eq 4, section IIIA)



The rate constant was originally found (126) to be

$$\log k_4 = 13.3 - (61.0/\theta)$$

on the basis of an assumed  $A$  factor, whereas the revised figure from aniline-carrier experiments (113) is

$$\log k_4 = 14.3 - (66.0/\theta)$$

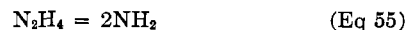
It follows that  $D(\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{-CH}_3)$  can be taken to be  $66$  kcal. The errors should not exceed  $\pm 2$  kcal.

B. NITROGEN-CONTAINING COMPOUNDS

1. Hydrazines

a.  $D(\text{NH}_2\text{-NH}_2)$

The pyrolysis of hydrazine yields direct information on  $D(\text{NH}_2\text{-NH}_2)$  since the decomposition occurs *via* the reaction



A reinvestigation of this reaction by the toluene-carrier technique (108) revealed a considerable pres-

sure effect upon the rate constants, which the original investigator (179) failed to detect. At 15 mm pressure the revised rate constant was found to be

$$\log k_{55} = 11.70 - (54.2/\theta)$$

Since the activation energy was obtained in the pressure-sensitive region a correction of 3 kcal was made to obtain  $E_{\infty} = 57$  kcal, which was identified with  $D(\text{NH}_2\text{-NH}_2)$ . The correction was later amended (113) to 2 kcal which means that  $D(\text{NH}_2\text{-NH}_2)$  can now be taken as 56 kcal with estimated errors of  $\pm 2$  kcal.

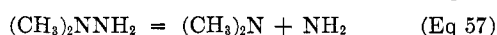
Several shock-tube studies of the decomposition of hydrazine have been reported, and the most recent (135) supports a limiting high-pressure rate constant of

$$\log k_{55} = 13.0 - (54/\theta)$$

which is in substantial agreement with the revised toluene-carrier data.

b.  $D(\text{CH}_3\text{NH-NH}_2)$  and  $D((\text{CH}_3)_2\text{N-NH}_2)$

Toluene-carrier studies of the decompositions



were reported (108) at the same time as that for the decomposition of hydrazine described above. The rate constants were shown to be

$$\log k_{56} = 13.19 - (51.9/\theta)$$

$$\log k_{57} = 13.22 - (49.6/\theta)$$

and both were independent of pressure. Thus  $D(\text{CH}_3\text{NH-NH}_2) = 51.9$  kcal and  $D((\text{CH}_3)_2\text{N-NH}_2) = 49.6$  kcal, with estimated errors of  $\pm 1$  to  $\pm 2$  kcal. A rate constant of

$$\log k = 7.8 - (28.7/\theta)$$

has been reported (49) for the decomposition of 1,1-dimethylhydrazine studied in a flow system with helium as carrier gas. This value is a composite quantity and cannot be identified with reaction 57.

c.  $D(\text{C}_6\text{H}_5\text{NH-NH}_2)$

The aniline-carrier technique has yielded results (113) on the pyrolysis



such that

$$\log k_{58} = 11.8 - (40.0/\theta)$$

and hence

$$D(\text{C}_6\text{H}_5\text{NH-NH}_2) = 40 \pm 2 \text{ kcal}$$

d.  $D(\text{N-N})$  in Other Hydrazines

The toluene-carrier method failed to provide kinetic information on the decompositions of 1,2-dimethyl-

and tetramethylhydrazine (108). It appears that the system is only successful with hydrazines that decompose to yield  $\text{NH}_2$  radicals, which form ammonia by the abstraction of a hydrogen atom from the carrier gas. The fate of the methylamino radicals is uncertain, but it is likely that they undergo heterogeneous reactions. From the results so far established for the decomposition of the hydrazines it is possible to calculate the heats of formation of the radicals  $\text{NH}_2$ ,  $\text{NHCH}_3$ , and  $\text{N}(\text{CH}_3)_2$ , and hence, from the heats of formation of the parent hydrazines, the  $D(\text{N-N})$  values which could not be obtained experimentally. This is a typical procedure for calculating bond dissociation energies once heats of formation of the radicals are known. From  $D(\text{NH}_2\text{-NH}_2) = 56$  kcal it follows that

$$\Delta H_f^\circ(\text{NH}_2) = \frac{1}{2}[D(\text{NH}_2\text{-NH}_2) + \Delta H_f^\circ(\text{N}_2\text{H}_4)] = 39.3 \text{ kcal}$$

while from  $D(\text{C}_6\text{H}_5\text{NH-NH}_2) = 40.0$  kcal we have

$$\Delta H_f^\circ(\text{NH}_2) = D(\text{C}_6\text{H}_5\text{NH-NH}_2) -$$

$$\Delta H_f^\circ(\text{C}_6\text{H}_5\text{NH}) + \Delta H_f^\circ(\text{C}_6\text{H}_5\text{NHNH}_2) = 41.3 \text{ kcal}$$

$\Delta H_f^\circ(\text{C}_6\text{H}_5\text{NH})$  was assumed to be 47.6 kcal (see section VB2),  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{NHNH}_2) = 48.9$  kcal (3), and  $\Delta H_f^\circ(\text{N}_2\text{H}_4) = 22.5$  kcal (94). From the two determinations a value of  $\Delta H_f^\circ(\text{NH}_2) = 40 \pm 2$  kcal is suggested.

The heats of formation of the two methylamino radicals can now be obtained from the pyrolysis data on the hydrazines and the equation

$$\Delta H_f^\circ(\text{R}_1\text{R}_2\text{N}) = D(\text{R}_1\text{R}_2\text{N-NH}_2) - \Delta H_f^\circ(\text{NH}_2) + \Delta H_f^\circ(\text{R}_1\text{R}_2\text{NNH}_2)$$

by making use of the deduced value of  $\Delta H_f^\circ(\text{NH}_2) = 40$  kcal. The data are summarized in Table VII.

TABLE VII  
CALCULATION OF HEATS OF FORMATION OF  
METHYLAMINO RADICALS

Compound	$D(\text{R}_1\text{R}_2\text{N-NH}_2)$ , kcal	$\Delta H_f^\circ(\text{R}_1\text{R}_2\text{NNH}_2)$ , kcal	Ref	$\Delta H_f^\circ(\text{R}_1\text{R}_2\text{N})$ , kcal
$\text{CH}_3\text{NHNH}_2$	51.9	22.4	11	34.4
$(\text{CH}_3)_2\text{NNH}_2$	49.6	19.7	11	29.3

The bond dissociation energies in the other hydrazines are now calculated from the equation

$$D(\text{R}_1\text{R}_2\text{N-NR}_3\text{R}_4) = \Delta H_f^\circ(\text{R}_1\text{R}_2\text{N}) + \Delta H_f^\circ(\text{R}_3\text{R}_4\text{N}) - \Delta H_f^\circ(\text{R}_1\text{R}_2\text{NNR}_3\text{R}_4)$$

The values listed in Table VIII for the methyl hydrazines have been deduced in this way (108). The value for the N-N bond dissociation energy in hydrazobenzene has been calculated from  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{NH}) = 47.6$  kcal (see section VB2) and is included for comparison. The extremely low value obtained,  $D$ -



TABLE VIII  
CALCULATED  $D(N-N)$  VALUES IN HYDRAZINES

Compound	$D(N-N)$ , kcal	$\Delta H_f^\circ$ (compound), kcal	Ref
$CH_3NH-NHCH_3$	47	21.6	11
$(CH_3)_2N-N(CH_3)_2$	42	16.6	51
$(CH_3)_2N-NHCH_3$	44	19.2	51
$C_6H_5NH-NHC_6H_5$	22	73	46

$(C_6H_5NH-NHC_6H_5) = 22$  kcal, casts considerable doubt on the thermochemical data (46).

The estimated errors are about  $\pm 5$  kcal in any of these calculated values, but the errors in the differences are less since some of the uncertainties cancel out. These kinetically determined dissociation energies for N-N bonds in methylhydrazines, form a self-consistent pattern and show the general trends expected for methyl substitution, by analogy with C-C or O-O bonds. Values obtained from electron impact studies on methylhydrazines (76) confirm this general trend, but owing to the limitations of the method the detailed values listed here are to be preferred.

## 2. Anilines

### a. $D(C_6H_5NH-CH_3)$ and $D(C_6H_5N(CH_3)-CH_3)$

Values for these bond dissociation energies have been obtained from aniline-carrier (56, 113) studies of the decomposition reactions



The rate constants are

$$\log k_{59} = 13.4 - (60.0/\theta)$$

$$\log k_{60} = 12.9 - (57.0/\theta)$$

leading to  $D(C_6H_5NH-CH_3) = 60$  and  $D(C_6H_5N(CH_3)-CH_3) = 57$  kcal with estimated errors of between  $\pm 1$  and  $\pm 2$  kcal. From the heats of formation of the methylanilines (66, 203) ( $\Delta H_f^\circ(C_6H_5NHCH_3) = 21.6$  and  $\Delta H_f^\circ(C_6H_5N(CH_3)_2) = 20.1$  kcal) the heats of formation of the anilino and N-methylanilino radicals are computed to be 47.6 and 43.1 kcal, respectively.

### b. $D(C_6H_5NH-H)$ and $D(C_6H_5N(CH_3)-H)$

These bond strengths can be calculated (113) from the heats of formation of the anilino and N-methylanilino radicals, determined above, and the heats of formation of the compounds. Taking  $\Delta H_f^\circ(C_6H_5NH_2) = 19.6$  kcal (3) and  $\Delta H_f^\circ(C_6H_5NHCH_3) = 21.6$  kcal (66) gives  $D(C_6H_5NH-H) = 80 \pm 3$  and  $D(C_6H_5N(CH_3)-H) = 74 \pm 3$  kcal.

### c. $D(C_6H_5-NR_2)$

Values are readily obtainable (108) where R = H or  $CH_3$  from the heats of formation of the amino radicals, as calculated above, and the heat of formation

of the phenyl radical ( $\Delta H_f^\circ(C_6H_5) = 72$  kcal). The data are summarized in Table IX. Maximum errors are estimated at  $\pm 4$  kcal.

TABLE IX  
CALCULATED VALUES OF  $D(C_6H_5-NR_2)$

Bond	$\Delta H_f^\circ$ - (compound), kcal	Ref	$D$ - ( $C_6H_5-NR_2$ ), kcal
$C_6H_5-NH_2$	19.6	3	92
$C_6H_5-NHCH_3$	21.6	66	85
$C_6H_5-N(CH_3)_2$	20.1	203	81

## 3. Amines

The N-H and N- $CH_3$  bond strengths listed in Table X have been calculated (108) from the previously determined heats of formation of the amino radicals.

TABLE X  
CALCULATED BOND DISSOCIATION ENERGIES IN AMINES

Bond	$\Delta H_f^\circ$ (compound), kcal	Ref	$D$ , kcal
$NH_2-H$	-11.0	164	103
$CH_3NH-H$	-5.1	105	92
$(CH_3)_2N-H$	-4.5	105	86
$CH_3-NH_2$	-5.1	105	79
$CH_3-NHCH_3$	-4.5	105	73
$CH_3-N(CH_3)_2$	-5.5	101	69

The estimated errors are between  $\pm 2$  and  $\pm 3$  kcal.

The pyrolyses of benzylamine and N-methylbenzylamine have been studied (108) by the toluene-carrier technique and the values  $D(C_6H_5CH_2-NH_2) = 60$  and  $D(C_6H_5CH_2-NHCH_3) = 58$  kcal reported (108). This determination of  $D(C_6H_5CH_2-NH_2)$  leads to a much lower value for  $\Delta H_f^\circ(NH_2)$  than that recommended here, but the heat of formation of benzylamine used in the calculation is almost certainly wrong (108). Unfortunately the heat of formation of N-methylbenzylamine is unknown, otherwise  $D(C_6H_5CH_2-NHCH_3) = 58$  kcal would serve as a check on the heat of formation of either the benzyl or the methylamino radical.

## 4. Nitriles

### a. $D(H-CN)$ and $D(CN-CN)$

Results on the decomposition of cyanogen from shock-tube studies are conflicting. Knight and Rink (120) investigated the reaction



by X-ray densitometer measurements of the density ratios across the shock wave as a function of shock velocity. The change in gas density reflects the change in temperature arising from the dissociation reaction.  $D_0(CN-CN)$  was deduced to be  $145 \pm 6$  kcal leading to  $\Delta H_f^\circ(CN) = 109$  kcal and  $D_0(H-CN) = 129$  kcal. In the same study this value of  $D_0(H-CN)$  was confirmed by the shock-wave decomposition of HCN.

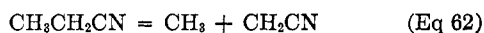
Reaction 61 has been studied (199) by a second shock-

tube method, which involved measuring the concentration of cyano radicals by spectrophotometric analysis. The value  $D_0(\text{CN-CN}) = 125 \pm 8$  kcal was reported, in considerable disagreement with the other determination.

Further evidence in support of the high values was put forward almost simultaneously with the second shock-tube study. From a mass spectrometric study (29) of the vapor in equilibrium with graphite and nitrogen at temperatures of 2200–2500°K it was shown that  $\Delta H_f^\circ(\text{CN}) = 109 \pm 3$  kcal. The weight of evidence certainly appears to favor the higher values, although these have not been established beyond reasonable doubt. The values discussed above refer to 0°K but corrections to 298°K hardly seem warranted at this stage in view of the large uncertainties involved.

b.  $D(\text{CNCH}_2\text{-H})$  and  $D(\text{CNCH}_2\text{-CH}_3)$

These quantities are related since there is no direct kinetic determination of  $D(\text{CNCH}_2\text{-H})$  and it must be calculated from  $\Delta H_f^\circ(\text{CNCH}_2)$  which follows from a knowledge of  $D(\text{CNCH}_2\text{-CH}_3)$ . Here again the aniline-carrier technique has been employed to determine  $D(\text{CNCH}_2\text{-CH}_3)$ . The decomposition of ethylnitrile has been shown to occur (95) *via* the reaction



with a rate constant of

$$\log k_{62} = 14.1 - (72.7/\theta)$$

This gives  $D(\text{CNCH}_2\text{-CH}_3) = 72.7$  kcal and, from  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{CN}) = 11.5$  kcal (183), leads to  $\Delta H_f^\circ(\text{CNCH}_2) = 50.2$  kcal. Likewise from  $\Delta H_f^\circ(\text{CH}_3\text{CN}) = 21.0$  kcal (162) it can be deduced that  $D(\text{CNCH}_2\text{-H}) = 81.3$  kcal, and hence the difference ( $D(\text{CNCH}_2\text{-H}) - D(\text{CNCH}_2\text{-CH}_3)$ ) is 8.6 kcal. It has been argued (95) that this difference should be close to 13 kcal, in comparison with other ( $D(\text{C-H}) - D(\text{C-CH}_3)$ ) differences, for compounds in which the H atom and  $\text{CH}_3$  radical are attached to a  $\text{CH}_2$  group. It was further concluded (95) that the most probable source of error in these determinations was in the value of  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{CN})$  used to calculate  $\Delta H_f^\circ(\text{CNCH}_2)$ . Thus the value

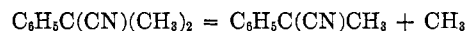
$$D(\text{CNCH}_2\text{-H}) = D(\text{CNCH}_2\text{-CH}_3) + 13 = 86 \text{ kcal}$$

was recommended as the best available. This gives  $\Delta H_f^\circ(\text{CH}_2\text{CN}) = 55$  kcal, but is in poor agreement with the electron impact determination of  $D(\text{CNCH}_2\text{-H}) \geq 79$  kcal (150). It would seem best to accept  $D(\text{CNCH}_2\text{-H}) = 86 \pm 3$  kcal as a tentative value.

c.  $D((\text{CH}_3)_2\text{C}(\text{CN})\text{-CH}_3)$  and  $D(\text{C}_6\text{H}_5\text{C}(\text{CN})(\text{CH}_3)\text{-CH}_3)$

Values of  $D((\text{CH}_3)_2\text{C}(\text{CN})\text{-CH}_3) = 70$  kcal and  $D(\text{C}_6\text{H}_5\text{C}(\text{CN})(\text{CH}_3)\text{-CH}_3) = 54$  kcal were reported from aniline-carrier pyrolyses of the nitriles (95).

As the authors point out, however, the latter value must be accepted with caution since it was not unambiguously shown that the decomposition occurred *via* the reaction

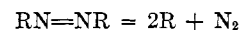


5. Azo Compounds

Although the kinetics of the decompositions of several azo and tetrazene compounds have been investigated (77), it appears that the activation energies ( $E_a$ ) cannot be identified with bond dissociation energies in these molecules. If the decompositions occur by a two-stage mechanism



then the first and second bond dissociation energies,  $D_1 = D(\text{RN}_2\text{-R})$  and  $D_2 = D(\text{N}_2\text{-R})$ , are defined as the enthalpy changes of reactions 63 and 64, respectively. The sum ( $D_1 + D_2$ ) can be calculated from the enthalpy change for the over-all reaction



if the heat of formation of the azo compound is known. In all cases where this information is available it turns out that  $E_a$  is considerably greater than ( $D_1 + D_2$ ). Gowenlock, Jones, and Snelling (77) have concluded that these compounds decompose by a "three-fragment" split.

Upper limits for  $D_1$  values in several azo compounds have been reported from electron impact studies (78), and these confirm that there is no direct relation between the activation energy ( $E_a$ ) for the decomposition and  $D_1$ .

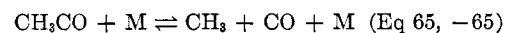
C. OXYGEN-CONTAINING COMPOUNDS

1. Aldehydes

a.  $D(\text{HCO-H})$  and  $D(\text{CH}_3\text{CO-H})$

There are no direct kinetic determinations of these quantities. Substantial information on  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  has been accumulated, however, and consequently indirectly on  $D(\text{CH}_3\text{CO-H})$ . Since  $D(\text{CH}_3\text{CO-H})$  is closely related to  $D(\text{HCO-H})$ , it is best to consider both bond dissociation energies under the same heading.

The situation regarding  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  has recently been summarized (107). One kinetic method of determining  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  depends on measuring the activation energies of the reactions



In a detailed investigation of reaction 65, by the photolysis of acetone in the presence of hydrogen iodide (146), the limiting high-pressure activation energy was shown to be  $E_{65(\infty)} = 15$  kcal. The original data (39) on the activation energy of reaction -65 was revised by photolyzing azomethane in admixture with

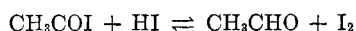
carbon monoxide (107) and yielded  $E_{-65(\infty)} = 5$  kcal. From these two results we have

$$\Delta H_{65,-65} = D(\text{CH}_3\text{-CO}) = E_{65} - E_{-65} = 10.6 \text{ kcal}$$

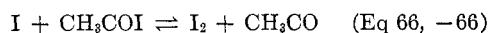
allowing for the change in standard states.  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  is then deduced from

$$\Delta H_{65,-65} = \Delta H_f^\circ(\text{CH}_3) + \Delta H_f^\circ(\text{CO}) - \Delta H_f^\circ(\text{CH}_3\text{CO})$$

and taking  $\Delta H_f^\circ(\text{CH}_3) = 34.0$  kcal gives  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -3$  kcal. This is in reasonable agreement with the value  $\Delta H_f^\circ(\text{CH}_3\text{CO}) \cong -5$  kcal which can be calculated from results (143) on photoionization mass spectrometry of acetyl compounds. The original authors (143) deduced  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -6.5$  kcal, but this is based on  $D_0(\text{CH}_3\text{-H}) = 101$  kcal. A second kinetic determination of  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  has been carried out by O'Neal and Benson (147) who studied the over-all reaction



By following the rate of formation of iodine spectrophotometrically they were able to obtain an activation energy of  $E_{66} = 14$  kcal for the reaction



From the relation

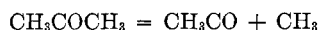
$$D(\text{CH}_3\text{CO-I}) = D(\text{I-I}) + E_{66} - E_{-66}$$

$D(\text{CH}_3\text{CO-I})$  was calculated to be 50.7 kcal by assuming  $E_{-66} = 0$ .  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  can then be calculated from the relation

$$D(\text{CH}_3\text{CO-I}) = \Delta H_f^\circ(\text{CH}_3\text{CO}) + \Delta H_f^\circ(\text{I}) - \Delta H_f^\circ(\text{CH}_3\text{COI})$$

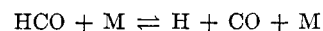
O'Neal and Benson (147) suggest a value of  $\Delta H_f^\circ(\text{CH}_3\text{COI}) = -31.4$  kcal leading to  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -6.3$  kcal. From these three determinations, Kerr and Calvert (107) proposed a value of  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -4 \pm 2$  kcal, and this has recently been endorsed (72) and will be adopted here.

Earlier attempts (45, 185) to determine  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  involved the pyrolysis of acetone by the toluene-carrier technique, according to the reaction



for which an activation energy of about 72 kcal was reported. If  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  is  $-4$  kcal, then from thermochemistry  $D(\text{CH}_3\text{CO-CH}_3)$  should be nearer 82 kcal. It now seems likely that the rate constants for the pyrolysis of acetone have been measured in the pressure-dependent region, so that the high-pressure activation energy may be considerably greater than the experimental value. Returning to  $D(\text{CH}_3\text{CO-H})$ , this dissociation energy is calculated to be 88 kcal from  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -4$  kcal and  $\Delta H_f^\circ(\text{CH}_3\text{CHO}) = -39.7$  kcal (84).

By analogy with the acetyl radical,  $\Delta H_f^\circ(\text{HCO})$  could be obtained from a kinetic study of the reactions



Unfortunately accurate kinetic data for these reactions are lacking because the systems developed for studying the acetyl formation and decomposition reactions are much more difficult to apply to the formyl reactions. Since there is no reliable experimental value of  $\Delta H_f^\circ(\text{HCO})$ , it must be estimated from an assumed value of  $D(\text{HCO-H})$ . Several authors (38, 146, 191) have suggested that  $D(\text{HCO-H}) \cong D(\text{CH}_3\text{CO-H})$  which now means  $D(\text{HCO-H}) = 88$  kcal. A rough check on this assumption can be made by working back to the results on  $D(\text{H-CO})$ . From  $D(\text{HCO-H}) \cong 88$  kcal it follows that  $\Delta H_f^\circ(\text{HCO}) \cong 8$  kcal, and hence

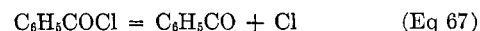
$$D(\text{H-CO}) = \Delta H_f^\circ(\text{H}) + \Delta H_f^\circ(\text{CO}) - \Delta H_f^\circ(\text{HCO}) \cong 18 \text{ kcal}$$

It was previously shown that  $D(\text{CH}_3\text{-CO}) = 10.6$  kcal so that  $(D(\text{H-CO}) - D(\text{CH}_3\text{-CO}))$  is estimated to be about 8 kcal. Within the experimental errors, this is the expected difference (191) between  $D(\text{C-H})$  and  $D(\text{C-CH}_3)$  and would indicate the general correctness of the above arguments.

In conclusion the values recommended are  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -4 \pm 2$  kcal,  $\Delta H_f^\circ(\text{HCO}) = 8 \pm 2$  kcal,  $D(\text{CH}_3\text{CO-H}) = D(\text{HCO-H}) = 88 \pm 2$  kcal. If these values are accepted, the long-standing controversy (38, 119) regarding the "high" or "low" value of  $D(\text{H-CO})$  could seem to be settled in favor of the "low" value, *i.e.*,  $D(\text{H-CO}) \cong 18$  kcal.

#### b. $D(\text{C}_6\text{H}_5\text{CO-H})$

A calculated value is available from  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CO})$ . The pyrolysis of benzyl chloride has been studied (184) by the toluene-carrier technique.



The rate constant was reported as

$$\log k_{67} = 15.4 - (73.6/\theta)$$

so that from  $D(\text{C}_6\text{H}_5\text{CO-Cl}) = 73.6$  kcal and  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{COCl}) = -28.9$  kcal (41),  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CO})$  is calculated to be 15.8 kcal. A similar value can be deduced from less accurate results on the pyrolysis of benzoyl bromide (124).  $D(\text{C}_6\text{H}_5\text{CO-H})$  then becomes 74 kcal, taking  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CHO}) = -6$  kcal (84). The errors are estimated as  $\pm 5$  kcal.

## 2. Ketones

The pyrolytic method has failed to yield reliable information on bond dissociation energies in ketones. The pyrolysis of acetone was considered in section VC1, and the pyrolyses of other lower aliphatic ketones have been shown to be complex processes (57). Schon

TABLE XI  
 KINETIC DATA ON  $\Delta H_f^\circ(\text{CH}_3\text{O})$ 

$\text{CH}_3\text{OX}$	$\Delta H_f^\circ(\text{CH}_3\text{OX}),$ kcal	Ref	$\Delta H_f^\circ(\text{X}),$ kcal	$E_{69},$ kcal	Ref	$\Delta H_f^\circ(\text{CH}_3\text{O}),$ kcal
$\text{CH}_3\text{ONO}$	-15.6	158	21.6	36.5	83	-0.7
$\text{CH}_3\text{ONO}_2$	-28.6	81	8.0	39.5	83	2.9
				38.4	81	1.4
$\text{CH}_3\text{OOCH}_3$	-30.0	81	...	36.1	87	3.1
	-31.6	21	...	36.1	87	2.3

 TABLE XII  
 KINETIC DATA ON  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{O})$ 

$\text{C}_2\text{H}_5\text{OX}$	$\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OX}),$ kcal	Ref	$\Delta H_f^\circ(\text{X}),$ kcal	$E_{69},$ kcal	Ref	$\Delta H_f^\circ(\text{C}_2\text{H}_5\text{O}),$ kcal
$\text{C}_2\text{H}_5\text{ONO}$	-24.2	83	21.6	37.7	83	-8.1
$\text{C}_2\text{H}_5\text{ONO}_2$	-36.8	83	8.0	36.4	83	-8.4
$\text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$	-47.8	21	...	34.1	87	-6.7

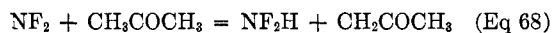
and Szwarc (169) and Clark and Pritchard (45) have indicated the difficulties involved in identifying activation energies for the decompositions of aromatic ketones with bond dissociation energies, arising from "three-fragment" splits of these molecules.

a.  $D(\text{CH}_3\text{CO}-\text{CH}_3)$

The best available value of this bond strength is derived from the heats of formation of the radicals; taking  $\Delta H_f^\circ(\text{CH}_3) = 34.0$ ,  $\Delta H_f^\circ(\text{CH}_3\text{CO}) = -4$ , and  $\Delta H_f^\circ(\text{CH}_3\text{COCH}_3) = -51.7$  kcal (84) gives  $D(\text{CH}_3\text{CO}-\text{CH}_3) = 82$  kcal with estimated errors of  $\pm 3$  kcal.

b.  $D(\text{CH}_3\text{COCH}_2-\text{H})$

An upper limit of  $D(\text{CH}_3\text{COCH}_2-\text{H}) = 92$  kcal has been obtained (86) from an activation energy of  $E_{69} = 19.5$  kcal for the reaction



The method was identical with that described in section IIIB. The errors involved in this determination are not likely to exceed  $\pm 3$  kcal.

### 3. Alcohols

In an excellent review, published in 1959, Gray and Williams (83) dealt at length with the thermochemistry and reactivities of alkoxy radicals. Few experimental results have been published since then which substantially alter the position concerning  $\Delta H_f^\circ(\text{RO})$  and  $D(\text{RO}-\text{H})$  values.

The  $\Delta H_f^\circ(\text{RO})$  values recommended by Gray and Williams (83) for the lower aliphatic alkoxy radicals are mainly based on kinetic determinations. The method involves the pyrolyses of compounds of the type ROX



where X = OR, NO, or NO<sub>2</sub> and R = alkyl radical. Assuming zero activation energy for the reverse reaction it follows that

$$\Delta H_{69} = E_{69} = \Delta H_f^\circ(\text{RO}) + \Delta H_f^\circ(\text{X}) - \Delta H_f^\circ(\text{ROX})$$

so that  $\Delta H_f^\circ(\text{RO})$  is obtained from the activation energy of the decomposition reaction, provided the heats of formation of the compound (ROX) and the radical (X) are known.

a.  $D(\text{CH}_3\text{O}-\text{H})$

The problem here is to ascertain the most acceptable value of  $\Delta H_f^\circ(\text{CH}_3\text{O})$  since there are no direct determinations of  $D(\text{CH}_3\text{O}-\text{H})$ . The data from the pyrolytic method have been summarized by Gray (81) and are shown in Table XI.

Gray (81) proposes  $\Delta H_f^\circ(\text{MeO}) = 2$  kcal and suggests probable errors of  $\pm 2$  kcal, both of which are perfectly reasonable in view of the evidence at hand. This result is slightly different from the original value (83) and gives  $D(\text{CH}_3\text{O}-\text{H}) = 102 \pm 2$  kcal.

b.  $D(\text{C}_2\text{H}_5\text{O}-\text{H})$

The relevant pyrolytic data, leading to  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{O})$ , are summarized in Table XII. Gray and Williams (83) adopted the value  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{O}) = -8.5$  kcal giving  $D(\text{C}_2\text{H}_5\text{O}-\text{H}) = 99$  kcal, but from the amended value of  $D(\text{CH}_3\text{O}-\text{H})$  it would now seem better to accept the results from the peroxide decomposition, *i.e.*,  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{O}) = -6.7$  kcal and  $D(\text{C}_2\text{H}_5\text{O}-\text{H}) = 102$  kcal. The estimated errors are about  $\pm 2$  kcal.

c.  $D(n-\text{C}_3\text{H}_7\text{O}-\text{H})$

Here again kinetic evidence has been obtained from the pyrolyses of the nitrite, nitrate, and peroxide as shown in Table XIII. In keeping with  $\Delta H_f^\circ(\text{CH}_3\text{O})$  and  $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{O})$  there is a case for accepting  $\Delta H_f^\circ(n-\text{C}_3\text{H}_7\text{O})$  from the peroxide data; hence  $\Delta H_f^\circ(n-\text{C}_3\text{H}_7\text{O}) = -11 \pm 2$  kcal and  $D(n-\text{C}_3\text{H}_7\text{O}-\text{H}) = 103 \pm 2$  kcal are adopted here.

d.  $D(t-\text{C}_4\text{H}_9\text{O}-\text{H})$

The kinetic evidence for  $\Delta H_f^\circ(t-\text{C}_4\text{H}_9\text{O})$  is based solely on the pyrolysis of di-*t*-butyl peroxide and since

TABLE XIII  
 KINETIC DATA ON  $\Delta H_f^\circ(n\text{-C}_3\text{H}_7\text{O})$ 

$n\text{-C}_3\text{H}_7\text{OX}$	$\Delta H_f^\circ(\text{C}_3\text{H}_7\text{OX})$ , kcal	Ref	$\Delta H_f^\circ(\text{X})$ , kcal	$E_{69}$ , kcal	Ref	$\Delta H_f^\circ(n\text{-C}_3\text{H}_7\text{O})$ , kcal
$n\text{-C}_3\text{H}_7\text{ONO}$	-31.2	83	21.6	37.7	83	-15.1
$n\text{-C}_3\text{H}_7\text{ONO}_2$	-41.6	83	8.0	37.6	83	-12.0
$(n\text{-C}_3\text{H}_7\text{O})_2$	-57.8	21	...	36.5	88	-10.7

the activation energy for the pyrolysis has recently been redetermined (16), this necessitates a slight alteration to  $\Delta H_f^\circ(t\text{-C}_4\text{H}_9\text{O})$ . Hence from  $E_{69} = 37.4$  kcal for reaction 69 involving di-*t*-butyl peroxide, and from  $\Delta H_f^\circ(t\text{-C}_4\text{H}_9\text{O})_2 = -85.5$  kcal (21),  $\Delta H_f^\circ(t\text{-C}_4\text{H}_9\text{O})$  becomes  $-24.1 \pm 2$  kcal and  $D(t\text{-C}_4\text{H}_9\text{O-H}) = 103 \pm 2$  kcal, taking  $\Delta H_f^\circ(t\text{-C}_4\text{H}_9\text{OH}) = -74.9$  kcal (84).

e.  $D(i\text{-C}_3\text{H}_7\text{O-H})$ ,  $D(n\text{-C}_4\text{H}_9\text{O-H})$ ,

$D(i\text{-C}_4\text{H}_9\text{O-H})$ , and  $D(\text{sec-C}_4\text{H}_9\text{O-H})$

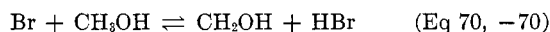
No new data have been published on the heats of formation of the radicals, which alter the position summarized by Gray and Williams (83); see data in Table XIV. The bond dissociation energies are slightly amended by taking revised figures (84) for the heats of formation of the alcohols.

 TABLE XIV  
 $\Delta H_f^\circ(\text{RO})$  AND  $D(\text{RO-H})$  FOR ALIPHATIC ALCOHOLS

ROH	$\Delta H_f^\circ(\text{RO})$ , kcal	$\Delta H_f^\circ(\text{ROH})$ , kcal	$D(\text{RO-H})$ , kcal
$i\text{-C}_3\text{H}_7\text{OH}$	-15	-65.4	103
$n\text{-C}_4\text{H}_9\text{OH}$	-17	-66.9	102
$i\text{-C}_4\text{H}_9\text{OH}$	-18	-67.9	102
$\text{sec-C}_4\text{H}_9\text{OH}$	-20	-70.1	102

f.  $D(\text{HOCH}_2\text{-H})$  and  $D(\text{HOCH}(\text{CH}_3)\text{-H})$

Values have been obtained from the bromination reactions



Buckley and Whittle (35) determined  $E_{70} = 6.2$  kcal, while Tarr and Whittle (188) found  $E_{71} = 5.0$  kcal. The reverse reactions have not been studied but the authors made the reasonable assumption that  $E_{-70} = E_{-71} = 2$  kcal and hence deduced  $D(\text{HOCH}_2\text{-H}) = 92$  kcal and  $D(\text{HOCH}(\text{CH}_3)\text{-H}) = 90$  kcal from the expression

$$D(\text{HOCH}_2\text{-H}) = D(\text{HBr}) + E_{70} - 2$$

The errors are estimated at about  $\pm 2$  kcal but the difference ( $D(\text{HOCH}_2\text{-H}) - D(\text{HOCH}(\text{CH}_3)\text{-H})$ ) should be more accurate than this.

g.  $D(\text{R-OH})$

A few values, calculated from the heats of formation of the radicals and the alcohols, are listed in Table XV. The errors are estimated to be about  $\pm 2$  kcal.

 TABLE XV  
 CALCULATED VALUES OF  $D(\text{R-OH})$ 

R	$\Delta H_f^\circ(\text{R})$ , kcal	$\Delta H_f^\circ(\text{OH})$ , kcal	$\Delta H_f^\circ(\text{ROH})$ , kcal	Ref	$D(\text{R-OH})$ , kcal
$\text{CH}_3$	34.0	9.3	-48.1	84	91
$\text{C}_2\text{H}_5$	25.7	9.3	-56.2	84	91
$i\text{-C}_3\text{H}_7$	17.6	9.3	-65.4	84	92
$t\text{-C}_4\text{H}_9$	6.8	9.3	-74.9	84	91

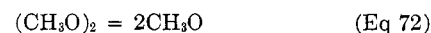
#### 4. Ethers and Esters

Gray and Williams (83) calculated bond dissociation energies for a few of these compounds from the heats of formation of the radicals. These calculations are now in need of revision owing to the changes in the values of the heats of formation of the radicals, particularly the alkyl and acyl radicals. The data are given in Tables XVI and XVII.

#### 5. Peroxides

##### a. $D(\text{CH}_3\text{O-OCH}_3)$

The kinetics of the reaction



have been studied by following the rate of disappearance of the peroxide with an infrared absorption spectrometer (87) and lead to the rate constant

$$\log k_{72} = 15.38 - (36.1/\theta)$$

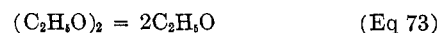
Thus  $D(\text{CH}_3\text{O-OCH}_3)$  can be taken to be 36.1 kcal. The errors are estimated at  $\pm 1$  kcal.

##### b. $D(\text{C}_2\text{H}_5\text{O-OC}_2\text{H}_5)$

Three original sets of data (89, 141, 159) on the pyrolysis of diethyl peroxide have been combined (87) to yield

$$\log k_{73} = 14.2 - (34.1/\theta)$$

for the reaction



This result is now generally accepted and hence  $D(\text{C}_2\text{H}_5\text{O-OC}_2\text{H}_5) = 34.1 \pm 1$  kcal.

##### c. $D(n\text{-C}_3\text{H}_7\text{O-O-}n\text{-C}_3\text{H}_7)$

The early data (88) on the decomposition of this peroxide lead to

$$\log k_{74} = 15.4 - (36.5/\theta)$$

for the reaction

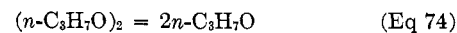


TABLE XVI  
 CALCULATED VALUES OF  $D(\text{RO}-\text{R}_1)$ 

ROR <sub>1</sub>	$\Delta H_f^\circ(\text{R}_1)$ , kcal	$\Delta H_f^\circ(\text{RO})$ , kcal	$\Delta H_f^\circ(\text{ROR}_1)$ kcal	Ref	$D(\text{RO}-\text{R}_1)$ , kcal
CH <sub>3</sub> OCH <sub>3</sub>	34.0	2.0	-44.3	84	80
C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	25.7	-6.7	-60.4	84	79
<i>i</i> -(C <sub>3</sub> H <sub>7</sub> OC <sub>3</sub> H <sub>7</sub> )	17.6	-15	-76.4	83	79
CH <sub>3</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	38	2.0	-22.3	83	52

 TABLE XVII  
 CALCULATED VALUES OF  $D(\text{RCO}-\text{OR}_1)$ 

RCOOR <sub>1</sub>	$\Delta H_f^\circ(\text{RCO})$ , kcal	$\Delta H_f^\circ(\text{OR}_1)$ , kcal	$\Delta H_f^\circ(\text{RCOOR}_1)$ , kcal	Ref	$D(\text{RCO}-\text{OR}_1)$ , kcal
CH <sub>3</sub> COOCH <sub>3</sub>	-4	2	-99.2	83	97
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	-4	-6.7	-106.6	83	96
CH <sub>3</sub> COO- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	-4	-11.0	-112.8	83	98
CH <sub>3</sub> COO- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	-4	-15	-115.8	83	97
CH <sub>3</sub> COO- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	-4	-17	-118.9	83	98
CH <sub>3</sub> COO- <i>i</i> -C <sub>4</sub> H <sub>9</sub>	-4	-18	-121.1	83	99
HCOOCH <sub>3</sub>	8	2	-83.6	83	94
C <sub>6</sub> H <sub>5</sub> COOCH <sub>3</sub>	15.8	2	-71.7	83	90
C <sub>6</sub> H <sub>5</sub> COOC <sub>2</sub> H <sub>5</sub>	15.8	-6.7	-79.1	83	88

and this value is still adopted (21, 87). It follows that  $D(n\text{-C}_3\text{H}_7\text{O}-\text{O}-n\text{-C}_3\text{H}_7) = 36.5$  kcal with probable errors of  $\pm 1$  kcal.



The precise rate constant for the decomposition



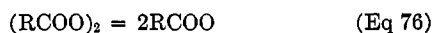
has been in contention for many years. There seems to have been a clarification of the position, however, by Batt and Benson (16) who have reinvestigated reaction 75 by measuring the pressure change in a static system and by a detailed analysis of the products, involving gas chromatography. The previously reported scatter in the rate constants was shown to be due to temperature gradients in the reaction vessels. The rate constant was found to be

$$\log k_{75} = 15.6 - (37.4/\theta)$$

and this is the best available value. Accordingly  $D(\textit{t}\text{-C}_4\text{H}_9\text{O}-\text{O}-\textit{t}\text{-C}_4\text{H}_9) = 37.4 \pm 1$  kcal.



The pyrolyses of acetyl, propionyl, and butyryl peroxides by the toluene-carrier technique have been re-



ported (160, 161) and the activation energies are usually accepted as the bond dissociation energies,  $D(\text{RCOO}-\text{OOCR})$ . The results are summarized in Table XVIII. The errors are estimated at about  $\pm 2$  kcal. It was later shown (173) that the activation energy for the decomposition of isobutryl peroxide in isooctane solution was 27 kcal, and this has been interpreted as showing the occurrence of a "three-fragment" decomposition, and hence the activation energy

 TABLE XVIII  
 DATA ON  $D(\text{RCOO}-\text{OOCR})$  FROM REACTION 76

(RCOO) <sub>2</sub>	Log A <sub>76</sub>	$D(\text{RCOO}-\text{OOCR})$ , kcal	Ref
(CH <sub>3</sub> COO) <sub>2</sub>	14.3	29.5	160
(C <sub>2</sub> H <sub>5</sub> COO) <sub>2</sub>	14.4	30.0	161
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> COO) <sub>2</sub>	14.3	29.6	161

should not be identified with  $D(\textit{i}\text{-C}_3\text{H}_7\text{COO}-\text{OOC}\textit{i}\text{-C}_3\text{H}_7)$ .

### 6. Hydroperoxides

The bond dissociation energies  $D(\text{RO}-\text{OH})$  for methyl, ethyl, *n*-propyl, and *t*-butyl hydroperoxides have been calculated (21) from the heats of formation of the alkoxy radicals and the heats of formation of the hydroperoxides. Apart from ethyl and *t*-butyl hydroperoxides, the heats of formation of the lower alkyl hydroperoxides have not been measured, owing to experimental difficulties, but they can be calculated from the rule of additivity of group properties developed by Benson and Buss (26) and should be accurate to about  $\pm 1$  kcal. The data for the calculation of  $D(\text{RO}-\text{OH})$  values are summarized in Table XIX.

 TABLE XIX  
 CALCULATED  $D(\text{RO}-\text{OH})$  VALUES

RO	$\Delta H_f^\circ(\text{RO})$ , kcal	$\Delta H_f^\circ(\text{ROOH})$ , kcal	Ref	$D(\text{RO}-\text{OH})$ , kcal
CH <sub>3</sub> O	2	-32.1	21	43
C <sub>2</sub> H <sub>5</sub> O	-6.7	-40.2	21	43
<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	-11.0	-45.2	21	44
<i>t</i> -C <sub>4</sub> H <sub>9</sub> O	-24.1	-58.6	21	44

It should be noted that the final results are slightly different from those originally calculated (21) owing to the revised value of  $\Delta H_f^\circ(\text{OH}) = 9.3$  kcal.

Kirk (115) has reported data for the pyrolysis of methyl hydroperoxide by the toluene-carrier technique, based on the analysis of dibenzyl, and results are also available (116) on the pyrolyses of ethyl, isopropyl, and *t*-butyl hydroperoxides from similar experiments involving benzene as the carrier gas and based on the analysis of biphenyl. The Arrhenius parameters for the homogeneous decompositions of the hydroperoxides are listed in Table XX.

TABLE XX  
ARRHENIUS PARAMETERS FOR DECOMPOSITION  
OF HYDROPEROXIDES

ROOH	Log A	E, kcal	Ref
CH <sub>3</sub> OOH	11	32	115
C <sub>2</sub> H <sub>5</sub> OOH	13.4	37.7	116
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OOH	15.2	40.0	116
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OOH	13.7	37.8	116

It is obvious that the activation energies are much too low to be equated to the bond dissociation energies,  $D(\text{RO-OH})$ , listed in Table XIX. It seems unlikely that the measured rates of the decompositions are seriously in error so it appears (21) that the mechanisms are not as simple as has been assumed.

TABLE XXI  
CALCULATED VALUES OF  $D(\text{RCOO-H})$

(RCOO) <sub>2</sub>	$D(\text{RCOO-OOCR}),$ kcal	$\Delta H_f^\circ((\text{RCOO})_2),$ kcal	Ref	$\Delta H_f^\circ(\text{RCOO}),$ kcal	$\Delta H_f^\circ(\text{RCOOH}),$ kcal	Ref	$D(\text{RCOO-H}),$ kcal
(CH <sub>3</sub> COO) <sub>2</sub>	29.5	-119	102	-45	-104.5	102	112
(C <sub>2</sub> H <sub>5</sub> COO) <sub>2</sub>	30.0	-138	102	-54	-111.4	102	110
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> COO) <sub>2</sub>	29.6	-150	102	-60	-110.4	102	103

### 7. Acids

#### a. $D(\text{C}_6\text{H}_5\text{CH}_2\text{-COOH})$ and $D((\text{C}_6\text{H}_5)_2\text{CH-COOH})$

An experimental value of  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-COOH})$  has been deduced from a toluene-carrier study (14) of the reaction



for which the rate constant was found to be

$$\log k_{77} = 12.9 - (55/\theta)$$

Hence  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-COOH}) = 55$  kcal, with estimated errors of about  $\pm 2$  kcal. A value of  $D((\text{C}_6\text{H}_5)_2\text{CH-COOH}) = 52$  kcal was obtained by the same authors (15), but since the mechanism was not clearly established this must be regarded as tentative.

#### b. $D(\text{RCOO-H})$

Calculated values for acetic, propionic, and *n*-butyric acids have been derived (102) from the heats of formation of the RCOO radicals

$$D(\text{RCOO-H}) = \Delta H_f^\circ(\text{RCOO}) + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{RCOOH})$$

which in turn are derived from the pyrolyses of the peroxides

$$D(\text{RCOO-OOCR}) = 2\Delta H_f^\circ(\text{RCOO}) - \Delta H_f^\circ((\text{RCOO})_2)$$

These calculations are possible since the heats of formation of the acids and the peroxides are known. The data are given in Table XXI. The errors are estimated to be approximately  $\pm 4$  kcal.

### D. SULFUR-CONTAINING COMPOUNDS

#### 1. Sulfides

##### a. $D(\text{HS-H})$

A thermochemical value is available from  $\Delta H_f^\circ(\text{HS})$  which can be calculated from  $D(\text{S-H})$  and  $\Delta H_f^\circ(\text{S})$ . The heat of formation of the gaseous sulfur atom has been in dispute for many years (50), but recent mass spectrometric studies on sulfides (47) have confirmed the value  $D_{298}(\text{S-S}) = 100$  kcal, which supports the result  $\Delta H_f^\circ(\text{S}) = 65.7$  kcal (175). From the equation

$$D(\text{S-H}) = \Delta H_f^\circ(\text{S}) + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{HS})$$

and the value  $D_{298}(\text{S-H}) = 82.3$  kcal (103) it follows that  $\Delta H_f^\circ(\text{HS}) = 35.5$  kcal. Taking  $\Delta H_f^\circ(\text{H}_2\text{S}) = -4.8$  kcal this means that  $D(\text{HS-H}) = 92$  kcal.

A kinetic value of  $D(\text{HS-H})$  can also be obtained via  $\Delta H_f^\circ(\text{HS})$  since this has been determined from the pyrolysis of benzyl sulfide. The reaction



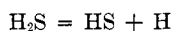
has been investigated (167) by the toluene-carrier technique and found to have a rate constant of

$$\log k_{78} = 13.5 - (53/\theta)$$

The heat of formation of gaseous benzyl sulfide has been determined (132) to be 21.9 kcal, and hence taking  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45$  kcal (see section VA4) this yields  $\Delta H_f^\circ(\text{HS}) = 29.9$  kcal and  $D(\text{HS-H}) = 87$  kcal. Mackle and McClean (132) calculated  $\Delta H_f^\circ(\text{HS}) = 34.9$  kcal by taking  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 40$  kcal, but as shown in section VA4 this value is incorrect.

In principle  $\Delta H_f^\circ(\text{HS})$  should also be obtainable from the pyrolyses of methyl and ethyl sulfides, but toluene-carrier studies of these decompositions (167) have proved to be too complex for the determinations of  $D(\text{HS-CH}_3)$  and  $D(\text{HS-C}_2\text{H}_5)$ .

The value  $D(\text{HS-H}) = 85.6$  kcal was deduced from a kinetic study of the pyrolysis of dimethyl ether catalyzed by hydrogen sulfide (136). The over-all reaction was followed by pressure measurements and the kinetics of the reaction



unravelling from a steady-state treatment of the proposed mechanism involving over a dozen reactions. This determination of  $D(\text{HS-H})$  would seem to be too indirect to be reliable.

The value  $\Delta H_f^\circ(\text{HS}) \leq 33.7$  kcal, corresponding to  $D(\text{HS-H}) \leq 90.6$  kcal, has been reported (148) from electron impact studies on sulfides.

The present position regarding  $D(\text{HS-H})$  is not well defined. The values to be considered are 92 kcal from thermochemical calculations based on  $D(\text{H-S})$ , 87 kcal from the kinetics of the pyrolysis of benzyl sulfide, and 90 kcal from electron impact results. The range of values is almost covered by  $90 \pm 2$  kcal, which is adopted here, but the situation is less satisfactory than this would imply and obviously more work is required.

#### b. $D(\text{CH}_3\text{S-H})$

The results are again conflicting. The pyrolysis of methyl benzyl sulfide



has been studied (32) by the toluene-carrier technique and found to have a rate constant of

$$\log k_{79} = 13.48 - (51.5/\theta)$$

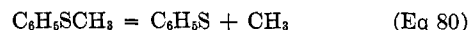
giving  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-SCH}_3) = 51.5$  kcal.  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{-CH}_2\text{SCH}_3)$  has been shown (131) to be 19.0 kcal, and hence taking  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 45$  kcal it can be shown that  $\Delta H_f^\circ(\text{CH}_3\text{S}) = 25.5$  kcal. It follows that  $D(\text{CH}_3\text{S-H})$  is 83.1 kcal from  $\Delta H_f^\circ(\text{CH}_3\text{SH}) = -5.5$  kcal. Mackle and Mayrick (131) took  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{-CH}_2) = 40$  kcal and calculated  $\Delta H_f^\circ(\text{CH}_3\text{S}) = 30.5$  kcal, but, as shown in section VA4,  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  should be taken as 45 kcal.

Palmer and Lossing (148) have determined  $\Delta H_f^\circ(\text{CH}_3\text{S}) \leq 31.8$  and  $D(\text{CH}_3\text{S-H}) \leq 89.4$  kcal from electron impact studies, both in serious disagreement with the kinetic results. Furthermore the electron impact results indicate a much smaller difference, ( $D(\text{HS-H}) - D(\text{CH}_3\text{S-H})$ ) than the kinetic results.

It seems unlikely that  $D(\text{HS-H})$  should exceed  $D(\text{CH}_3\text{S-H})$  by more than 2 kcal and if  $D(\text{HS-H})$  is taken as  $90 \pm 2$  kcal this means  $D(\text{CH}_3\text{S-H}) \geq 88$  kcal and  $\Delta H_f^\circ(\text{CH}_3\text{S}) \geq 30.4$  kcal. It must be emphasized, however, that these are only tentative values and that more experimental work is necessary.

#### c. $D(\text{C}_6\text{H}_5\text{S-H})$ and $D(\text{C}_6\text{H}_5\text{S-CH}_3)$

The pyrolysis of methyl phenyl sulfide has been studied by the toluene-carrier technique (13)



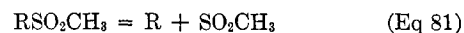
and found to have a rate constant of

$$\log k_{80} = 14.48 - (60/\theta)$$

from which it follows that  $D(\text{C}_6\text{H}_5\text{S-CH}_3) = 60$  kcal. The value  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{SCH}_3) = 23.5$  kcal has been confirmed (131); hence, from  $\Delta H_f^\circ(\text{CH}_3) = 34.0$  kcal,  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{S})$  is calculated to be 49.5 kcal.  $D(\text{C}_6\text{H}_5\text{S-H})$  can now be calculated to be 75 kcal since  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{SH})$  is known to be 26.7 kcal (133). It must be pointed out that these values of  $D(\text{C}_6\text{H}_5\text{S-CH}_3)$ ,  $D(\text{C}_6\text{H}_5\text{S-H})$ , and  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{S})$  are tentative, since the mechanism of the pyrolysis of methyl phenyl sulfide was not rigorously established. Calculations of other  $D(\text{C}_6\text{H}_5\text{S-R})$  bond strengths would hardly seem justified at this stage.

#### 2. Sulfones

$D(\text{R-SO}_2\text{CH}_3)$  values for R = methyl, allyl, and phenyl have been reported (36) from toluene-carrier pyrolyses of the sulfones



At the same time the heats of formation of the sulfones were obtained (37). Both sets of the data are summarized in Table XXII.

TABLE XXII  
KINETIC AND THERMOCHEMICAL DATA FOR SULFONES (36, 37)

Sulfone	Log $A_{81}$	$(E_{81} =$ $D(\text{CH}_3\text{SO}_2\text{-R}),$ kcal	$\Delta H_f^\circ(\text{RSO}_2\text{CH}_3),$ kcal
$\text{CH}_3\text{SO}_2\text{CH}_3$	14.3	60.6	89.9
$\text{C}_6\text{H}_5\text{SO}_2\text{CH}_3$	14.1	47.7	73.5
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_3$	14.5	51.3	68.0

From the pyrolysis of dimethyl sulfone and  $\Delta H_f^\circ(\text{CH}_3) = 34.0$  kcal, the heat of formation of the radical  $\text{CH}_3\text{SO}_2$  is deduced to be  $-63.2$  kcal. Hence from the pyrolyses of the other two sulfones the heats of formation of the radicals R can now be derived from the expression

$$D(\text{R-SO}_2\text{CH}_3) = \Delta H_f^\circ(\text{R}) + \Delta H_f^\circ(\text{CH}_3\text{SO}_2) - \Delta H_f^\circ(\text{RSO}_2\text{CH}_3)$$

Thus  $\Delta H_f^\circ(\text{C}_6\text{H}_5) = 37.5$  kcal (see section VA2) and  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2) = 46.6$  kcal (see section VA4). The agreement between these calculated heats of formation of the allyl and benzyl radicals and values derived from other sources can be taken as a good indication of the reliability of the sulfone pyrolyses.

#### 3. Other Sulfur Compounds

Mackle (130) has reviewed the thermochemistry of sulfur-containing compounds and has calculated many bond dissociation energies from the heats of formation of the sulfide and alkyl sulfide radicals and the heats of



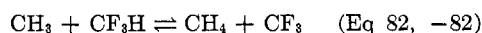
formation of the parent compounds. Until the heats of formation of the sulfur-containing radicals are known with more certainty, however, these calculated bond dissociation energies remain highly speculative.

#### E. HALOGEN-CONTAINING COMPOUNDS

##### 1. Fluoro Compounds

###### a. $D(\text{CF}_3\text{-H})$

Until recently the value  $D(\text{CF}_3\text{-H}) = 102$  kcal seemed established from the kinetics of the system

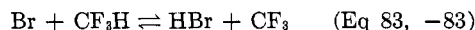


$E_{82} = 9.8$  kcal was determined (156) from the photolysis of hexadeuterioacetone in the presence of fluoroform, and in conjunction with the known value of  $E_{-82} = 10.3$  kcal it was concluded (156) that

$$D(\text{CF}_3\text{-H}) = D(\text{CH}_3\text{-H}) + E_{82} - E_{-82} = \\ (D(\text{CH}_3\text{-H}) - 0.5) \text{ kcal}$$

At the time  $D(\text{CH}_3\text{-H})$  was accepted as 102.5 kcal; hence,  $D(\text{CF}_3\text{-H})$  became 102 kcal.

Corbett, Tarr, and Whittle (48) subsequently investigated the thermal and photochemical bromination reactions of fluoroform



and deduced  $E_{83} = 23.5$  kcal. The activation energy for the reverse reaction ( $E_{-83}$ ) was assumed to be 1 kcal, and hence

$$D(\text{CF}_3\text{-H}) = D(\text{H-Br}) + 23.5 - 1$$

which, when corrected to 298°K, gave 109 kcal. The difficulties in accepting this higher value of  $D(\text{CF}_3\text{-H})$  have been outlined by Skinner (170). The large discrepancy between these two sets of results prompted further work on both systems.

Reaction 82 was reinvestigated (157), again by the photolysis of hexadeuterioacetone in the presence of fluoroform. The relevant reactions are Eq 82 and



For the purposes of hydrogen abstraction reactions, trideuteriomethyl radicals can be regarded as equivalent to methyl radicals. From the known value ( $E_{84} - 1/2E_{85}$ ) = 11.4 kcal and their experimental result ( $E_{84} - E_{82}$ ) = 1.2 kcal, Pritchard and Thommarson (157) deduced that  $E_{82} = (11.4 + 1/2E_{85} - 1.2)$  kcal. The reaction of trifluoromethyl radicals with methane, reaction -82, had been studied by photolyzing hexafluoroacetone in the presence of methane (12). The value ( $E_{-82} - 1/2E_{86}$ ) = 10.3 kcal was reported, where  $E_{86}$  is the activation energy of the reaction



This value has been substantially confirmed by a recent reinvestigation of the same system (1). Hence  $E_{-82} = (10.3 + 1/2E_{86})$  kcal, and from the relation for reactions 82 and -82

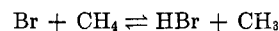
$$D(\text{CF}_3\text{-H}) = D(\text{CH}_3\text{-H}) + E_{82} - E_{-82}$$

it follows that

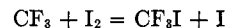
$$D(\text{CF}_3\text{-H}) = D(\text{CH}_3\text{-H}) + \\ (11.4 + 1/2E_{85} - 1.2) - (10.3 + 1/2E_{86}) = \\ D(\text{CH}_3\text{-H}) - 0.1 + 1/2E_{85} - 1/2E_{86}$$

$E_{85}$  is usually taken to be zero, but Pritchard and Thommarson (157) assumed a value of 1 kcal for the activation energy ( $E_{86}$ ) of the combination reaction of  $\text{CF}_3$  radicals, mainly on the basis of the temperature coefficient of the cross-combination reaction of  $\text{CH}_3$  and  $\text{CF}_3$  radicals. More recent results (71) have revealed an anomaly in this cross-combination reaction, and it now seems that  $E_{86}$  should be taken to be zero. Hence from the revised value of  $D(\text{CH}_3\text{-H}) = 104.0$  kcal it can be deduced that  $D(\text{CF}_3\text{-H}) = 103.9$  kcal.

The bromination of fluoroform was reexamined (187) by the competitive method (see section IIIB2) involving mixtures of  $\text{CH}_4$  and  $\text{C}_2\text{F}_5\text{H}$  and mixtures of  $\text{CF}_3\text{H}$  and  $\text{C}_2\text{F}_5\text{H}$ . The difference in reactivity between  $\text{CH}_4$  and  $\text{CF}_3\text{H}$  in bromination reactions is too great to compete them directly, so the problem is to find a suitable "bridge" compound, such as  $\text{C}_2\text{F}_5\text{H}$ , to compete with each. It was thus shown that  $E_{83} - E_{22} = 3.76$  kcal, where  $E_{22}$  refers to the reaction (Eq 22, -22)



This result has recently been confirmed (2) by taking  $n\text{-C}_3\text{F}_7\text{H}$  as another "bridge" compound between  $\text{CH}_4$  and  $\text{CF}_3\text{H}$  in competitive bromination experiments. The reverse of the bromination reaction of fluoroform, -83, has been studied by photolyzing hexafluoroacetone in the presence of hydrogen bromide-iodine mixtures (202). Assuming zero activation energy for the reaction



it was shown that  $E_{-83} = 3.0$  kcal and this is supported by subsequent results of Amphlett, Coomber, and Whittle (2). For reactions 83 and 22 the following relation applies

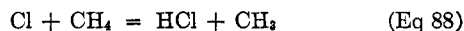
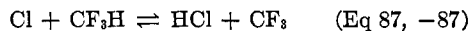
$$D(\text{CF}_3\text{-H}) - D(\text{CH}_3\text{-H}) = \\ (E_{83} - E_{22}) - (E_{-83} - E_{-22})$$

and in conjunction with the known value (61)  $E_{-22} = 1.4$  kcal it follows that

$$D(\text{CF}_3\text{-H}) = D(\text{CH}_3\text{-H}) + 2.2 = 106.2 \text{ kcal}$$

To check this revised determination, Amphlett, Coomber, and Whittle (2) have also studied competitive

chlorination of mixtures of  $\text{CF}_3\text{H}$  and  $\text{C}_2\text{F}_5\text{H}$  and mixtures of  $\text{CH}_4$  and  $\text{C}_2\text{F}_5\text{H}$ . A bridge compound is again necessary since  $\text{CF}_3\text{H}$  and  $\text{CH}_4$  have much too large a difference in reactivity toward chlorine atoms to be directly compared with accuracy. For the reactions



it was shown that  $E_{87} - E_{88} = 4.5$  kcal, and since  $E_{88}$  is known to be 3.9 kcal (122) it follows that  $E_{87} = 8.4$  kcal.  $D(\text{CF}_3\text{-H})$  can now be calculated from the relation

$$D(\text{CF}_3\text{-H}) - D(\text{H-Cl}) = E_{87} - E_{-87}$$

since  $E_{-87}$  was determined (2) to be 5.1 kcal by photolyzing hexafluoroacetone in the presence of HCl. This gives  $D(\text{CF}_3\text{-H}) = 106.3$  kcal on correction to 298°K, which agrees extremely well with the revised value from the bromination work. Amphlett, Coomber, and Whittle (2) propose  $106.2 \pm 0.5$  kcal, and, although this seems an optimistic estimate of the errors, the weight of evidence now favors this higher value, and we shall adopt here  $D(\text{CF}_3\text{-H}) = 106.2 \pm 1$  kcal.

#### b. $D(\text{CHF}_2\text{-H})$ and $D(\text{CH}_2\text{F-H})$

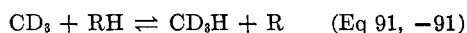
Upper limits have been placed on these bond dissociation energies from competitive bromination reactions (187). For the reactions



activation energies of  $E_{89} = 15.3$  and  $E_{90} = 14.8$  kcal were established from which it was deduced that  $D(\text{CHF}_2\text{-H}) \leq 102.8$  and  $D(\text{CH}_2\text{F-H}) \leq 103.3$  kcal. It was then reasonably assumed (187) that  $E_{-89} = E_{-90} = 2$  kcal, leading to  $D(\text{CHF}_2\text{-H}) = D(\text{CH}_2\text{F-H}) \cong 101$  kcal, but in view of the revised value of  $D(\text{CF}_3\text{-H}) = 106$ , these figures should be assigned substantial errors, say  $\pm 4$  kcal.

#### c. $D(\text{C}_2\text{F}_5\text{-H})$ and $D(n\text{-C}_3\text{F}_7\text{-H})$

The reactions involved here are



Pritchard and Thommarson (157) determined  $E_{91} = 9.5$  kcal for  $\text{C}_2\text{F}_5\text{H}$  and  $E_{91} = 9.1$  kcal for  $n\text{-C}_3\text{F}_7\text{H}$ , in the same study as the redetermination of  $D(\text{CF}_3\text{-H})$ . Furthermore, the activation energies  $E_{-91}$  have been shown to be 10.6 and 9.5 kcal for  $\text{R} = \text{C}_2\text{F}_5$  (152) and  $n\text{-C}_3\text{F}_7$  (69), respectively, on the assumption of zero activation energy for the recombination of the perfluoroalkyl radicals. Applying the relation

$$D(\text{R-H}) = D(\text{CH}_3\text{-H}) + E_{91} - E_{-91}$$

the values are deduced to be

$$D(\text{C}_2\text{F}_5\text{-H}) = 104 + 9.5 - 10.6 = 102.9 \text{ kcal}$$

$$D(n\text{-C}_3\text{F}_7\text{-H}) = 104 + 9.1 - 9.5 = 103.6 \text{ kcal}$$

The probable errors are  $\pm 2$  kcal and the recommended values are  $D(\text{C}_2\text{F}_5\text{-H}) = 103 \pm 2$  kcal and  $D(n\text{-C}_3\text{F}_7\text{-H}) = 104 \pm 2$  kcal. The value  $D(\text{C}_2\text{F}_5\text{-H}) \leq 102$  kcal has been obtained from competitive bromination studies (187) so the agreement is reasonably good.

#### d. $D(\text{CF}_3\text{-CF}_3)$

Tschuikow-Roux (200, 201) has determined  $D(\text{CF}_3\text{-CF}_3) \cong 93 \pm 4$  kcal, by studying the decomposition reaction in a single-pulse shock tube, and he has summarized other existing data on  $D(\text{CF}_3\text{-CF}_3)$  and  $\Delta H_f^\circ(\text{CF}_3)$ . A thermochemical value of  $D(\text{CF}_3\text{-CF}_3)$  is available since  $\Delta H_f^\circ(\text{CF}_3)$  can be calculated from  $D(\text{CF}_3\text{-H}) = 106.2$  kcal (see section VE1). Taking  $\Delta H_f^\circ(\text{CF}_3\text{H}) = -165.1$  kcal (175) leads to  $\Delta H_f^\circ(\text{CF}_3) = -111.0$  kcal, and hence from  $\Delta H_f^\circ(\text{C}_2\text{F}_6) = -303$  kcal (117) it follows that  $D(\text{CF}_3\text{-CF}_3) = 81$  kcal. The shock-tube result,  $D(\text{CF}_3\text{-CF}_3) = 93$  kcal, seems rather high in comparison with  $D(\text{CH}_3\text{-CH}_3) = 88$  kcal, but as previously noted (200) the heat of formation of hexafluoroethane may not be reliable. Until more work is done on these systems the value  $D(\text{CF}_3\text{-CF}_3) = 86 \pm 5$  kcal is recommended.

#### e. $D(\text{R-F})$

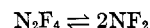
The best available estimates of the C-F bond dissociation energies in alkyl fluorides are derived from the heats of formation of the radicals and the parent compounds. The results are summarized in Table XXIII.

TABLE XXIII  
CALCULATED  $D(\text{R-F})$  VALUES

RF	$\Delta H_f^\circ(\text{R})$ , kcal	$\Delta H_f^\circ(\text{RF})$ , kcal	Ref	$D(\text{R-F})$ kcal
$\text{CH}_3\text{F}$	34.0	-55	23	108
$\text{C}_2\text{H}_5\text{F}$	25.7	-61	23	106
$n\text{-C}_3\text{H}_7\text{F}$	21.1	-66	123	106
$i\text{-C}_3\text{H}_7\text{F}$	17.6	-68	123	105
$\text{C}_6\text{H}_5\text{F}$	72	-26.5	166	117

#### f. $D(\text{NF}_2\text{-NF}_2)$ , $D(\text{NF}_2\text{-H})$ , and $D(\text{NF}_2\text{-F})$

An accurate value of  $D(\text{NF}_2\text{-NF}_2) = 19.9 \pm 0.5$  kcal has been determined (104) from equilibrium measurements on the system



This is one of the few free-radical systems in which the enthalpy change can be measured directly from equilibrium constants. The above value has been confirmed by mass spectrometric (92) and other studies (149).

Grzechowiak, Kerr, and Trotman-Dickenson (85) proposed a value of  $D(\text{NF}_2\text{-H}) = 72.6$  kcal on the basis of  $\alpha = 1.0$  in the Polanyi relation for the reaction of difluoroamino radicals with alkanes (section IV).

It now seems that this is probably a considerable underestimate. A thermochemical value of  $D(\text{NF}_2\text{-H})$  is available from  $\Delta H_f^\circ(\text{NF}_2)$ . Thus

$$\Delta H_f^\circ(\text{NF}_2) = 1/2(D(\text{NF}_2\text{-NF}_2) -$$

$$\Delta H_f^\circ(\text{N}_2\text{F}_4)) = 8.9 \text{ kcal}$$

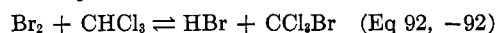
taking  $\Delta H_f^\circ(\text{N}_2\text{F}_4) = 2.0 \text{ kcal}$  (8). The value of  $\Delta H_f^\circ(\text{NF}_2\text{H})$  has not been reported, but a reasonable estimate has been interpolated (172) from  $\Delta H_f^\circ(\text{NH}_3) = -11 \text{ kcal}$  and  $\Delta H_f^\circ(\text{NF}_3) = -29.7 \text{ kcal}$ , leading to  $\Delta H_f^\circ(\text{NF}_2\text{H}) = -24 \text{ kcal}$ . It follows that  $D(\text{NF}_2\text{-H}) = 85 \text{ kcal}$  which is probably the best available estimate, but minimum errors of  $\pm 5 \text{ kcal}$  should be assigned.

Since  $\Delta H_f^\circ(\text{NF}_3)$  is known to be  $-30 \text{ kcal}$  (7),  $D(\text{NF}_2\text{-F})$  has been calculated (92, 114) to be  $58 \text{ kcal}$  with estimated errors of  $\pm 5 \text{ kcal}$ .

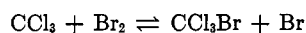
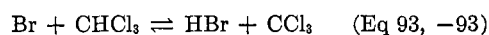
## 2. Chloro Compounds

### a. $D(\text{CCl}_3\text{-H})$

Benson (22) has reexamined the thermodynamics and kinetics of the system



originally studied by Sullivan and Davidson (177). The mechanism involves the reactions



and by taking new entropy data for the species concerned, a more precise value of  $\Delta H_{92,-92}$  has been deduced, leading to  $\Delta H_f^\circ(\text{CCl}_3\text{Br}) = -8.7 \text{ kcal}$ .

It was also possible to assign Arrhenius parameters to the elementary reactions of the mechanism from a detailed analysis of the kinetic data, on the basis of reasonable estimates of  $S^\circ(\text{CCl}_3)$  and  $C_p^\circ(\text{CCl}_3)$ . Hence it was shown that  $\Delta H_{93,-93} = 8.2 \pm 1 \text{ kcal}$  so that from the relation

$$D(\text{CCl}_3\text{-H}) - D(\text{H-Br}) = \Delta H_{93,-93}$$

it follows that  $D(\text{CCl}_3\text{-H}) = 95.7 \pm 1 \text{ kcal}$ , and thus  $\Delta H_f^\circ(\text{CCl}_3) = 18.6 \pm 2 \text{ kcal}$  from  $\Delta H_f^\circ(\text{CHCl}_3) = -25.0 \text{ kcal}$  (175).

### b. $D(\text{CCl}_3\text{-X})$

The values listed in Table XXIV have been calculated from  $\Delta H_f^\circ(\text{CCl}_3) = 18.6 \text{ kcal}$ , as deduced above, and the heats of formation of the compounds. The results are slightly different from those originally calculated (22) since a revised value of  $\Delta H_f^\circ(\text{CHCl}_3)$  has been used to calculate  $\Delta H_f^\circ(\text{CCl}_3)$ .

### c. $D(\text{R-Cl})$

$D(\text{R-Cl})$  values in alkyl chlorides are readily calculated from the heats of formation of the radicals and the alkyl chlorides. The data are given in Table XXV. The errors are estimated to be about  $\pm 2 \text{ kcal}$ .

TABLE XXIV  
CALCULATED VALUES OF  $D(\text{CCl}_3\text{-X})$

$\text{CCl}_3\text{X}$	$\Delta H_f^\circ$ , kcal	Ref	$D(\text{CCl}_3\text{-X})$ , kcal	Estimated errors, kcal
$\text{CCl}_3\text{F}$	-68	175	106	3
$\text{CCl}_4$	-25.9	175	73.4	2
$\text{CCl}_3\text{Br}$	-8.7	22	54.0	2

TABLE XXV  
CALCULATED VALUES OF  $D(\text{R-Cl})$

RCl	$\Delta H_f^\circ(\text{R})$ , kcal	$\Delta H_f^\circ(\text{RCl})$ , kcal	Ref	$D(\text{R-Cl})$ , kcal
$\text{CH}_3\text{Cl}$	34.0	-20.7	23	84
$\text{C}_2\text{H}_5\text{Cl}$	25.7	-26.7	23	81
<i>n</i> - $\text{C}_3\text{H}_7\text{Cl}$	21.1	-31.7	24	82
<i>i</i> - $\text{C}_3\text{H}_7\text{Cl}$	17.6	-34.6	24	81
<i>t</i> - $\text{C}_4\text{H}_9\text{Cl}$	6.8	-42.9	24	79

### d. $D(\text{C}_6\text{H}_5\text{CH}_2\text{-Cl})$

This bond dissociation energy has already been mentioned in connection with the determination of  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  (see section VA4).  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-Cl}) = 68 \text{ kcal}$  was determined by the toluene-carrier method (184), and the errors should not exceed  $\pm 2 \text{ kcal}$ .

### e. $D(\text{C}_6\text{H}_5\text{CO-Cl})$

The value  $D(\text{C}_6\text{H}_5\text{CO-Cl}) = 73.6 \text{ kcal}$ , determined by the toluene-carrier technique (184), was used in section VC1 to derive  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CO})$ . Since the determination of  $D(\text{C}_6\text{H}_5\text{CO-Cl})$  involved a high-temperature study, it should be assigned errors of  $\pm 3 \text{ kcal}$ .

## 3. Bromo Compounds

Szwarc and his co-workers have reported many C-Br bond dissociation energies, but, since most of them depend upon an assumed  $A$  factor for the decomposition reaction, they are not all considered here (see section IIIA).

### a. $D(\text{R-Br})$

As for the other alkyl halides, the best available values are probably those calculated from the heats of formation of the radicals, and listed in Table XXVI. The errors are estimated to be about  $\pm 2 \text{ kcal}$ .

TABLE XXVI  
CALCULATED VALUES OF  $D(\text{R-Br})$

RBr	$\Delta H_f^\circ(\text{R})$ , kcal	$\Delta H_f^\circ(\text{RBr})$ , kcal	Ref	$D(\text{R-Br})$ , kcal
$\text{CH}_3\text{Br}$	34.0	-9.5	23	70
$\text{C}_2\text{H}_5\text{Br}$	25.7	-16.3	24	69
<i>n</i> - $\text{C}_3\text{H}_7\text{Br}$	21.1	-21.2	24	69
<i>i</i> - $\text{C}_3\text{H}_7\text{Br}$	17.6	-23.5	24	68
<i>t</i> - $\text{C}_4\text{H}_9\text{Br}$	6.8	-29.5	24	63

### b. $D(\text{CH}_2=\text{CHCH}_2\text{-Br})$

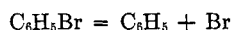
Although the pyrolysis of allyl bromide has been extensively studied by the toluene-carrier (181, 190) and other techniques (129), it is extremely doubtful

if the activation energy (45–48 kcal) can be identified with  $D(\text{C}_3\text{H}_5\text{-Br})$ . This point was discussed in connection with  $\Delta H_f^\circ(\text{C}_3\text{H}_5)$  in section VA2.

The pyrolyses of 3-bromopropyne and bromopropadiene, which have been reported (190) from toluene-carrier studies, are also unlikely to yield reliable values of the C-Br bond strengths in these molecules.

c.  $D(\text{C}_6\text{H}_5\text{-Br})$

An experimental value of this bond dissociation energy has been reported (186) from the toluene-carrier pyrolysis (Eq 42)



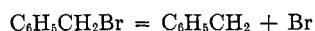
Thus from the rate constant

$$\log k_{42} = 13.3 - (70.9/\theta)$$

$D(\text{C}_6\text{H}_5\text{-Br})$  was deduced to be 70.9 kcal. As shown in section VA4, however, the value of  $\Delta H_f^\circ(\text{C}_6\text{H}_5)$  which can be derived from this bond dissociation energy seems rather low and, accordingly,  $D(\text{C}_6\text{H}_5\text{-Br}) = 71 \pm 4$  kcal is recommended.

d.  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-Br})$

The pyrolyses data on reaction 48



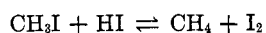
reported from several toluene-carrier studies (125, 127, 181) support  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-Br}) = 51$  kcal. This result can be accepted with confidence since it leads to a value of  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$  consistent with the best available value (see section VA4). Errors of  $\pm 1$  kcal therefore seem reasonable.

#### 4. Iodo Compounds

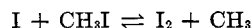
Pyrolytic determinations of  $D(\text{R-I})$  values in alkyl iodides have not been successful. Benson (20) has considered the kinetics of the pyrolyses of alkyl iodides and concludes that fission of the R-I bonds is not a rate-determining step, so that no information on  $D(\text{R-I})$  can be gleaned from these systems.

a.  $D(\text{CH}_3\text{-I})$

The most reliable kinetic determination of this bond dissociation energy is based on the system



which has been investigated by Flowers and Benson (64). The method, outlined in section IIIB1, leads to accurate kinetic data on reaction 10, -10



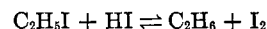
from which it was concluded that  $\Delta H_{10,-10} = 20.2$  kcal (see also section VA1).  $D(\text{CH}_3\text{-I})$  can then be calculated to be 56.3 kcal from

$$D(\text{CH}_3\text{-I}) - D(\text{I-I}) = \Delta H_{10,-10}$$

The uncertainty is about  $\pm 1$  kcal.

b.  $D(\text{C}_2\text{H}_5\text{-I})$

A kinetic study of the system



again leads to the most reliable value of  $D(\text{C}_2\text{H}_5\text{-I})$ . Hartley and Benson (91) have determined  $E_{94} = 16.9$  kcal for the reaction



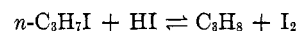
Hence by assuming  $E_{-94} = 0$ ,  $\Delta H_{94,-94}$  becomes 16.9 kcal, and from the equation

$$D(\text{C}_2\text{H}_5\text{-I}) = D(\text{I-I}) + \Delta H_{94,-94}$$

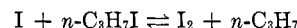
it follows that  $D(\text{C}_2\text{H}_5\text{-I}) = 53.0 \pm 1$  kcal.

c.  $D(\text{R-I})$  in Higher Alkyl Iodides

Unfortunately accurate kinetic data on the HI-RI systems is lacking for alkyl iodides higher in the series than ethyl iodide. The original data of Ogg (145) on the system



have been recalculated (28, 176) and  $E_{31} = 18$  kcal deduced for reaction 31, -31



Assuming  $E_{-31} = 0$ ,  $\Delta H_{31,-31}$  becomes 18 kcal (see section VA2), and hence

$$D(n\text{-C}_3\text{H}_7\text{-I}) = D(\text{I-I}) + 18 = 54 \text{ kcal}$$

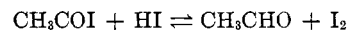
Minimum errors of  $\pm 2$  kcal must be assigned to this value. There is good agreement between this result and that which can be calculated from the heats of formation of the *n*-propyl radical and the iodide. Some other R-I bond strengths listed in Table XXVII can also be calculated in this way. The estimated errors are  $\pm 2$  kcal.

TABLE XXVII  
CALCULATED VALUES OF  $D(\text{R-I})$

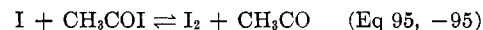
RI	$\Delta H_f^\circ(\text{R})$ , kcal	$\Delta H_f^\circ(\text{RI})$ , kcal	Ref	$D(\text{R-I})$ , kcal
<i>n</i> -C <sub>3</sub> H <sub>7</sub> I	21.1	-7.1	24	54
<i>i</i> -C <sub>3</sub> H <sub>7</sub> I	17.6	-9.9	24	53
<i>t</i> -C <sub>4</sub> H <sub>9</sub> I	6.8	-17.2	24	50

d.  $D(\text{CH}_3\text{CO-I})$

A determination has been reported (147) from a kinetic study of the system



The method was discussed in connection with  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  in section VC1. For the reaction



$E_{95}$  was shown to be 14.6 kcal, and by making the usual assumption that the reverse reaction, -95,

TABLE XXVIII  
 KINETIC AND THERMOCHEMICAL DATA ON PYROLYSES OF METAL ALKYLs

Compound	$E_a^a$	Log $A$	Ref	$D_1^a$	$D_2^a$	$D_3^a$	$\Delta H_f^\circ$ (compound) <sup>a</sup>	Ref	$\Delta H_f^\circ$ (metal atom) <sup>a</sup>	( $D_1 + D_2 + D_3$ ) <sup>a</sup>
Zn(CH <sub>3</sub> ) <sub>2</sub>	47.2	11.3	154	47	35 <sup>b</sup>	...	13.3	128	31.2	86
Cd(CH <sub>3</sub> ) <sub>2</sub>	45.8	11.9	153	46	22	...	26.4	128	26.8	68
Hg(CH <sub>3</sub> ) <sub>2</sub>	50.1	13.1	79, 153	50	12	...	20.8	128	14.7	62
Hg(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	42.5	14.1	42	43	3	...	20.0	128	14.7	46
Hg(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	48.3	11.9	194	48	...	...	...	...	...	...
Ga(CH <sub>3</sub> ) <sub>3</sub>	59.5	15.5	96	60	35 <sup>b</sup>	85	-9.1	128	69	180
In(CH <sub>3</sub> ) <sub>3</sub>	47.2	15.7	97	47	...	40(?) <sup>b</sup>	...	...	...	...
Cl <sub>2</sub> Sn(CH <sub>3</sub> ) <sub>2</sub>	56.1	13.5	155	56(?)	...	...	...	...	...	...
Sb(CH <sub>3</sub> ) <sub>3</sub>	57.0	15.2	155	57(?)	...	...	-9.2	128	63	174
Tl(CH <sub>3</sub> ) <sub>3</sub>	27.4	10.8	98	27	...	...	...	...	...	...
Bi(CH <sub>3</sub> ) <sub>3</sub>	44.0	14.0	155	44	...	...	45.8	128	49.5	106

<sup>a</sup> Units: kcal. <sup>b</sup> Experimental value.

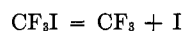
has zero activation energy it follows that  $\Delta H_{95,-95} = 14.6$  kcal and

$$D(\text{CH}_3\text{CO-I}) = D(\text{I-I}) + 14.6 = 50.7 \text{ kcal}$$

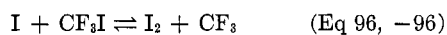
Since this result leads to a slightly low value of  $\Delta H_f^\circ(\text{CH}_3\text{CO})$  (see section VC1), it should be assigned errors of  $\pm 2$  kcal.

e.  $D(\text{CF}_3\text{-I})$

The pyrolysis reaction



has been studied (31) in static and flow systems in the presence of excess hydrogen iodide. The value  $D(\text{CF}_3\text{-I}) = 53.5$  kcal was obtained from  $E_{96} = 17.6$  kcal for the reaction



and the relation

$$D(\text{CF}_3\text{-I}) = D(\text{I-I}) + E_{96} - E_{-96}$$

by assuming a value of  $E_{-96}$  close to zero. It is difficult to assess the errors involved in this determination, as full experimental details are lacking, but since the method yields a reasonable value for the kinetic parameters of the analogous reaction involving  $\text{CH}_3\text{I}$ , the errors should not be greater than  $\pm 2$  kcal.

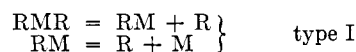
f.  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-I})$

Reference was made to this bond strength in section VA4 concerning  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CH}_2)$ . The determination  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-I}) = 39$  kcal reported from toluene-carrier experiments and corrected to 40.3 kcal by Benson and Buss (25) has been confirmed by pyrolysis studies in a flow system with hydrogen iodide as carrier gas (31). The value  $D(\text{C}_6\text{H}_5\text{CH}_2\text{-I}) = 40 \pm 1$  kcal (204) is acceptable.

F. METAL ALKYLs

The decompositions of these compounds can be complicated by "three-fragment" splits, such as occur

with azo compounds and some ketones (30), and hence two possible mechanisms have to be considered



An additional step is included in type I mechanisms involving trivalent metals. For type I mechanisms the activation energy ( $E_a = D(\text{RM-R})$ ) and the  $A$  factor is usually about "normal," whereas for type II mechanisms  $E_a > (D(\text{RM-R}) + D(\text{R-M}))$  and the  $A$  factor is "high." Obviously a type I mechanism must be established before the activation energy of the decomposition can be identified with the bond dissociation energy,  $D(\text{RM-R})$ , which is of interest here. Most of the kinetic information on the decompositions of metal alkyls has been obtained from toluene-carrier experiments. The data are listed in Table XXVIII for the decompositions of compounds where a type I mechanism seems reasonably certain. For trivalent metals ( $\text{MR}_3$ ),  $D_1$  corresponds to  $D(\text{R}_2\text{M-R})$ ,  $D_2$  to  $D(\text{RM-R})$ , and  $D_3$  to  $D(\text{R-M})$ . The sum ( $D_1 + D_2 + D_3$ ) is calculated from the expression

$$(D_1 + D_2 + D_3) = \Delta H_f^\circ(\text{M}) +$$

$$3\Delta H_f^\circ(\text{R}) - \Delta H_f^\circ(\text{MR}_3)$$

For divalent metals the corresponding equation for ( $D_1 + D_2$ ) applies. The values listed in Table XXVIII

 TABLE XXIX  
 HEATS OF FORMATION OF SOME GASEOUS ATOMS AT 298°K

Atom	$\Delta H_f^\circ$ , kcal	Errors, kcal	Atom	$\Delta H_f^\circ$ , kcal	Errors, kcal
H	52.10	0.06	Zn	31.2	0.5
C	170.9	0.45	Ga	69.0	
N	113.0	1	Br	26.74	0.07
O	59.56	0.03	Cd	26.75	0.2
F	18.86	0.2	Sb	63	2
S	65.65	0.6	I	25.54	0.01
Cl	28.92	0.03	Hg	14.65	0.02
			Bi	49.5	1

TABLE XXX  
 HEATS OF FORMATION OF RADICALS AT 298°K

Radical	$\Delta H_f^\circ$ , kcal	Estimated errors, kcal	Method of determination	Ref or section
CH	142	1	$D(\text{C-H}) = 81$	VA1
CH <sub>2</sub>	90	4	$D(\text{CH-H}) = 104$	VA1
CH <sub>3</sub>	34.0	1	Various including $D(\text{CH}_3\text{-H}) = 104.0$	VA1
C <sub>2</sub> H <sub>3</sub>	64	2	$D(\text{C}_2\text{H}_3\text{-H}) = 104$	VA2
C <sub>2</sub> H <sub>5</sub>	25.7	1	Various, including $D(\text{C}_2\text{H}_5\text{-H}) = 98.0$	VA1
C <sub>3</sub> H <sub>5</sub>	38	1	Various, including $D(\text{C}_3\text{H}_5\text{-H}) = 85$	VA2
<i>c</i> -C <sub>3</sub> H <sub>5</sub>	61	3	$D(\textit{c}\text{-C}_3\text{H}_5\text{-H}) = 101$	VA3
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	21	2	Various, including $D(\textit{n}\text{-C}_3\text{H}_7\text{-H}) = 98$	VA1
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	17.6	1	$D(\textit{i}\text{-C}_3\text{H}_7\text{-H}) = 94.5$	VA1
<i>c</i> -C <sub>4</sub> H <sub>7</sub>	49	3	$D(\textit{c}\text{-C}_4\text{H}_7\text{-H}) = 95$	VA3
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	17	2	$D(\textit{n}\text{-C}_4\text{H}_9\text{-H}) \cong 98$	...
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	14	2	$D(\textit{i}\text{-C}_4\text{H}_9\text{-H}) \cong 98$	...
<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	12.4	1	$D(\textit{sec}\text{-C}_4\text{H}_9\text{-H}) = 94.5$	VA1
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	6.8	1	$D(\textit{t}\text{-C}_4\text{H}_9\text{-H}) = 91.0$	VA1
<i>c</i> -C <sub>5</sub> H <sub>9</sub>	22	3	$D(\textit{c}\text{-C}_5\text{H}_9\text{-H}) = 93$	VA3
<i>neo</i> -C <sub>5</sub> H <sub>11</sub>	7.5	1	$D(\textit{neo}\text{-C}_5\text{H}_{11}\text{-H}) = 99.3$	VA1
C <sub>6</sub> H <sub>5</sub>	72	2	$D(\text{C}_6\text{H}_5\text{-H}) = 104$	VA4
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	12	3	$D(\textit{c}\text{-C}_6\text{H}_{11}\text{-H}) = 94$	VA3
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	45	1	Various, including $D(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 85$	VA4
C <sub>6</sub> H <sub>5</sub> CHCH <sub>3</sub>	33	2	$D(\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{-CH}_3) = 66$	VA4
CN	109	3	$D(\text{CN-CN}) = 145$	VB4
CH <sub>2</sub> CN	55	3	$D(\text{CNCH}_2\text{-CH}_3) = 86$	VB4
CH <sub>2</sub> NH	34.3	2	$D(\text{CH}_2\text{NH-NH}_2) = 51.9$	VB1
(CH <sub>3</sub> ) <sub>2</sub> N	29.3	2	$D((\text{CH}_3)_2\text{N-NH}_2) = 49.6$	VB1
C <sub>6</sub> H <sub>5</sub> NH	47.6	2	$D(\text{C}_6\text{H}_5\text{NH-CH}_3) = 60$	VB2
C <sub>6</sub> H <sub>5</sub> NCH <sub>3</sub>	43.1	2	$D(\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{-CH}_3) = 57$	VB2
CHO	8	2	$D(\text{HCO-H}) = 88$	VC1
CH <sub>2</sub> O	2	2	Various	VC3
COOH	-65?	...	$D(\text{C}_6\text{H}_5\text{CH}_2\text{-COOH}) = 55$	VC7
CH <sub>2</sub> OH	-8	3	$D(\text{HOCH}_2\text{-H}) = 92$	VC3
CH <sub>3</sub> CO	-4	2	Various	VC1
CH <sub>3</sub> CO <sub>2</sub>	-45	4	$D(\text{CH}_3\text{CO}_2\text{-O}_2\text{CCH}_3) = 29.5$	VC7
CH <sub>3</sub> CHOH	-18	3	$D(\text{HOCH}(\text{CH}_3)\text{-H}) = 90$	VC3
C <sub>2</sub> H <sub>5</sub> O	-6.7	2	Various	VC3
CH <sub>3</sub> COCH <sub>2</sub>	-12	3	$D(\text{CH}_3\text{COCH}_2\text{-H}) = 92$	VC2
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub>	-54	4	$D(\text{C}_2\text{H}_5\text{CO}_2\text{-O}_2\text{CC}_2\text{H}_5) = 30.0$	VC7
<i>n</i> -C <sub>3</sub> H <sub>7</sub> O	-11	2	Various	VC3
<i>i</i> -C <sub>3</sub> H <sub>7</sub> O	-15	2	Various	VC3
<i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub>	-60	4	$D(\textit{n}\text{-C}_3\text{H}_7\text{CO}_2\text{-O}_2\text{CC}_3\text{H}_7) = 29.6$	VC7
<i>n</i> -C <sub>4</sub> H <sub>9</sub> O	-17	2	Various	VC3
<i>i</i> -C <sub>4</sub> H <sub>9</sub> O	-18	2	Various	VC3
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> O	-20	2	Various	VC3
<i>t</i> -C <sub>4</sub> H <sub>9</sub> O	-24.1	2	$D(\textit{t}\text{-C}_4\text{H}_9\text{O-OC}_4\text{H}_9) = 37.4$	VC3
C <sub>6</sub> H <sub>5</sub> CO	16	3	$D(\text{C}_6\text{H}_5\text{CO-Cl}) = 73.6$	VC1
CF <sub>2</sub>	-35	10	Electron impact	134
CF <sub>3</sub>	-111	2	$D(\text{CF}_3\text{-H}) = 106$	VE1
CCl <sub>3</sub>	18.6	2	$D(\text{CCl}_3\text{-H}) = 95.7$	VE2
NH <sub>2</sub>	40	2	Various	VB1
NF <sub>2</sub>	8.9	2	$D(\text{NF}_2\text{-NF}_2) = 19.9$	VE1
HO	9.3	1	$D(\text{O-H}) = 102.4$	82
HO <sub>2</sub>	5	2	$D(\text{HO}_2\text{-H}) = 90$	65
HS	33?	...	$D(\text{HS-H}) = 90$	VD1
CH <sub>3</sub> S	30?	...	$D(\text{CH}_3\text{S-H}) = 88$	VD1
C <sub>6</sub> H <sub>5</sub> S	50?	...	$D(\text{C}_6\text{H}_5\text{S-CH}_3) = 60$	VD1
CH <sub>3</sub> SO <sub>2</sub>	-63.2	2	$D(\text{CH}_3\text{SO}_2\text{-CH}_3) = 61$	VD1

for  $(D_1 + D_2)$  or  $(D_1 + D_2 + D_3)$  are revised from the original data (128) to allow for the new values of  $\Delta H_f^\circ(\text{R})$ , as listed in Table XXX. The values for  $D_2$  are calculated from the experimental values of  $D_1$

(corresponding to the activation energy  $(E_a)$  of the decomposition) and the sum  $(D_1 + D_2)$  calculated from thermochemistry. In a few cases, experimental values of  $D_2$  are available which, in the case of a divalent

TABLE XXXI  
 BOND DISSOCIATION ENERGIES IN RADICALS

Bond	$D_{298}$ (calcd), kcal	$E_d$ , kcal	Ref	$E_{-d}$ , kcal	Ref	$D_{298}$ (exptl), kcal
OC-H	18					
OC <sub>2</sub> H-H	22					
CHCH-H	42					
CH <sub>2</sub> CH <sub>2</sub> -H	39	40	111			
CH <sub>2</sub> CH(CH <sub>2</sub> )-H	36	35	111			
CH <sub>2</sub> CHCH <sub>2</sub> -H	39	37	111			
CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>2</sub> )-H	36					
CH <sub>2</sub> CH <sub>2</sub> CHCH <sub>2</sub> -H	40					
(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>2</sub> )-H	35	31	111			
(CH <sub>3</sub> ) <sub>2</sub> CC <sub>2</sub> H-H	42					
CH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub>	26	34.5	111	8.6	34	26
CH <sub>2</sub> CH(CH <sub>2</sub> )-CH <sub>2</sub>	24	26	111	8.8	140	17
CH <sub>2</sub> CHCH <sub>2</sub> -CH <sub>2</sub>	27	24	111	8.8	140	15
(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>2</sub> )-CH <sub>2</sub>	23	32	6			
CH <sub>2</sub> CH <sub>2</sub> -C <sub>2</sub> H <sub>5</sub>	21	22	111	6.9	111	15
OC-CH <sub>3</sub>	12	15	146	5	107	10
OC <sub>2</sub> H-CH <sub>3</sub>	13	13	205			
CH <sub>2</sub> CO-CH <sub>3</sub>	31					
OC(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>3</sub>	6	11	137			
OC-C <sub>2</sub> H <sub>5</sub>	30					
O <sub>2</sub> C-CH <sub>3</sub>	-15					

metal, can be compared with the thermochemical value or, in the case of a trivalent metal, can be used to calculate  $D_3$ .

#### VI. HEATS OF FORMATION OF ATOMS AND RADICALS

The heats of formation of atoms at 298°K, which have been used in this review to calculate bond dissociation energies, are listed in Table XXIX. They are taken from the JANAF Tables (175) or a recent review (171).

Bond dissociation energies for diatomic molecules have been summarized by Benson (23).

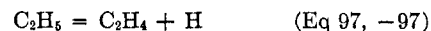
Table XXX lists the heats of formation of radicals, many of which have already been discussed where their determination is the only method of obtaining a bond dissociation energy. Also included are the heats of formation of a few simple radicals, which are sometimes required in thermochemical calculations, but which have been obtained from spectroscopic, mass spectrometric, or other nonkinetic methods. Brief indications are also given of the methods by which the values were obtained along with references either to preceding parts of the text or to sources not previously discussed. Values listed with a query are tentative. An up-to-date list of heats of formation of radicals is now published in the "Handbook of Chemistry and Physics" (112).

#### VII. BOND DISSOCIATION ENERGIES IN RADICALS

From the heats of formation of the radicals, listed in Table XXX, it is possible to calculate bond strengths in the radicals, *e.g.*

$$D(\text{CH}_2\text{CH}_2\text{-H}) = \Delta H_f^\circ(\text{C}_2\text{H}_4) + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{C}_2\text{H}_5) = 39 \text{ kcal}$$

Some of the more interesting examples, calculated in this way, are listed in Table XXXI. Occasionally the calculated value can be compared with an experimental value. Again taking the example of  $D(\text{CH}_2\text{-CH}_2\text{-H})$ , the reaction is



and hence the experimental value is obtained from the equation

$$D(\text{CH}_2\text{CH}_2\text{-H}) = \Delta H_{97,-97} = E_{97} - E_{-97}$$

if the activation energies of the decomposition ( $E_d$ ) and the reverse reaction ( $E_{-d}$ ) are known. The few available results on  $E_d$  and  $E_{-d}$  values are listed in Table XXXI.

#### VIII. BEST AVAILABLE VALUES OF BOND DISSOCIATION ENERGIES

A summary of the values recommended in this review is given in Table XXXII. Some bond dissociation energies from nonkinetic sources are also included where they are of particular interest, and these are supplemented by a reference and a brief indication of the method. A similar list is now available in the "Handbook of Chemistry and Physics" (112), and since this is revised annually it should prove to be a valuable source of up-to-date data.

ACKNOWLEDGMENTS.—The author is grateful to A. F. Trotman-Dickenson for his critical comments on the

TABLE XXXII  
 BEST AVAILABLE VALUES OF BOND DISSOCIATION ENERGIES

Bond	$D_{298}$ , kcal	Estimated errors, kcal	Bond	$D_{298}$ , kcal	Estimated errors, kcal
CH-H	108	6	C <sub>2</sub> H <sub>5</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	80	2
CH <sub>2</sub> -H	104	6	(CH <sub>3</sub> ) <sub>2</sub> CH-CH(CH <sub>3</sub> ) <sub>2</sub>	78	2
CH <sub>3</sub> -H	104.0	1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -CH <sub>3</sub>	70	2
CH <sub>2</sub> =CH-H	104	2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -C <sub>2</sub> H <sub>5</sub>	69	2
C <sub>2</sub> H <sub>5</sub> -H	98.0	1	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )-CH <sub>3</sub>	66	2
CH <sub>2</sub> =CHCH <sub>2</sub> -H	85	1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	67	2
<i>c</i> -C <sub>6</sub> H <sub>5</sub> -H	101	3	CN-CN	145	6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -H	98	2	CNCH <sub>2</sub> -CH <sub>3</sub>	73	2
(CH <sub>3</sub> ) <sub>2</sub> CH-H	94.5	1	(CH <sub>3</sub> ) <sub>2</sub> C(CN)-CH <sub>3</sub>	70	2
<i>c</i> -C <sub>4</sub> H <sub>7</sub> -H	95	3	C <sub>6</sub> H <sub>5</sub> C(CN)(CH <sub>3</sub> )-CH <sub>3</sub>	54	?
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )-H	94.6	1	CH <sub>3</sub> CO-CH <sub>3</sub>	82	3
(CH <sub>3</sub> ) <sub>3</sub> C-H	91.0	1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -COOH	55	2
<i>c</i> -C <sub>6</sub> H <sub>9</sub> -H	93	3	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH-COOH	52	?
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> -H	99.3	1	CF <sub>3</sub> -CF <sub>3</sub>	86	5
C <sub>6</sub> H <sub>5</sub> -N	104	2	CH <sub>3</sub> -NH <sub>2</sub>	79	3
<i>c</i> -C <sub>6</sub> H <sub>11</sub> -H	94	3	CH <sub>3</sub> -NHCH <sub>3</sub>	73	3
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -H	85	1	CH <sub>3</sub> -N(CH <sub>3</sub> ) <sub>2</sub>	69	3
<i>c</i> -C <sub>7</sub> H <sub>13</sub> -H	93	3	CH <sub>3</sub> -NHC <sub>6</sub> H <sub>5</sub>	60	2
H-CN	129	3	CH <sub>3</sub> -N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	57	2
CNCH <sub>2</sub> -H	86	3	C <sub>6</sub> H <sub>5</sub> -NH <sub>2</sub>	92	4
HCO-H	88	2	C <sub>6</sub> H <sub>5</sub> -NHCH <sub>3</sub>	85	4
HOCH <sub>2</sub> -H	92	2	C <sub>6</sub> H <sub>5</sub> -N(CH <sub>3</sub> ) <sub>2</sub>	81	4
CH <sub>3</sub> CO-H	88	2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -NH <sub>2</sub>	60	2
HOCH(CH <sub>3</sub> )-H	90	2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -NHCH <sub>3</sub>	58	2
CH <sub>3</sub> COCH <sub>2</sub> -H	92	3	CH <sub>3</sub> -OH	91	2
C <sub>6</sub> H <sub>5</sub> CO-H	74	5	C <sub>2</sub> H <sub>5</sub> -OH	91	2
CH <sub>2</sub> F-H	101	4	<i>i</i> -C <sub>2</sub> H <sub>7</sub> -OH	92	2
CHF <sub>2</sub> -H	101	4	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -OH	91	2
CF <sub>3</sub> -H	106	1	CH <sub>3</sub> O-CH <sub>3</sub>	80	5
C <sub>2</sub> F <sub>5</sub> -H	103	2	C <sub>2</sub> H <sub>5</sub> O-C <sub>2</sub> H <sub>5</sub>	79	5
<i>n</i> -C <sub>3</sub> F <sub>7</sub> -H	104	2	CH <sub>3</sub> O-CH <sub>2</sub> CH=CH <sub>2</sub>	52	5
CCl <sub>3</sub> -H	95.7	1	<i>i</i> -C <sub>2</sub> H <sub>7</sub> O-C <sub>2</sub> H <sub>7</sub>	79	5
NH <sub>2</sub> -H	103	2	CH <sub>2</sub> -F	108	3
CH <sub>3</sub> NH-H	92	3	C <sub>2</sub> H <sub>5</sub> -F	106	2
(CH <sub>3</sub> ) <sub>2</sub> N-H	86	3	<i>n</i> -C <sub>4</sub> H <sub>7</sub> -F	106	3
C <sub>6</sub> H <sub>5</sub> NH-H	80	3	<i>i</i> -C <sub>3</sub> H <sub>7</sub> -F	105	3
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> )-H	74	3	C <sub>6</sub> H <sub>5</sub> -F	117	5
NF <sub>2</sub> -H	85	5	CCl <sub>3</sub> -F	106	3
HO-H	119 <sup>a</sup>	1	C <sub>6</sub> H <sub>5</sub> S-CH <sub>3</sub>	60	?
CH <sub>3</sub> O-H	102	2	CH <sub>3</sub> SO <sub>2</sub> -CH <sub>3</sub>	60.6	1
C <sub>2</sub> H <sub>5</sub> O-H	102	2	CH <sub>3</sub> SO <sub>2</sub> -CH <sub>2</sub> CH=CH <sub>2</sub>	47.7	1
<i>n</i> -C <sub>3</sub> H <sub>7</sub> O-H	103	2	CH <sub>3</sub> SO <sub>2</sub> -CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	51.3	1
<i>i</i> -C <sub>2</sub> H <sub>7</sub> O-H	103	2	CH <sub>3</sub> -Cl	84	2
<i>n</i> -C <sub>4</sub> H <sub>9</sub> O-H	102	2	C <sub>2</sub> H <sub>5</sub> -Cl	81	2
<i>s</i> -C <sub>4</sub> H <sub>9</sub> O-H	102	2	<i>n</i> -C <sub>3</sub> H <sub>7</sub> -Cl	82	2
<i>i</i> -C <sub>4</sub> H <sub>9</sub> O-H	102	2	<i>i</i> -C <sub>3</sub> H <sub>7</sub> -Cl	81	2
<i>t</i> -C <sub>4</sub> H <sub>9</sub> O-H	103	2	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -Cl	79	2
HOO-H	90 <sup>b</sup>	2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -Cl	68	2
CH <sub>3</sub> COO-H	112	4	C <sub>6</sub> H <sub>5</sub> CO-Cl	74	3
C <sub>2</sub> H <sub>5</sub> COO-H	110	4	CCl <sub>3</sub> -Cl	73	2
<i>n</i> -C <sub>3</sub> H <sub>7</sub> COO-H	103	4	CH <sub>3</sub> Zn-CH <sub>3</sub>	47	2
HS-H	90	2	(CH <sub>3</sub> ) <sub>2</sub> Ga-CH <sub>3</sub>	60	2
CH <sub>3</sub> S-H	88	?	CH <sub>3</sub> -Br	70	2
C <sub>6</sub> H <sub>5</sub> S-H	75	?	C <sub>2</sub> H <sub>5</sub> -Br	69	2
BH <sub>3</sub> -BH <sub>3</sub>	37 <sup>c</sup>	4	<i>n</i> -C <sub>4</sub> H <sub>7</sub> -Br	69	2
BH <sub>3</sub> -CO	23 <sup>c</sup>	2	<i>i</i> -C <sub>3</sub> H <sub>7</sub> -Br	68	2
CH≡CH	230 <sup>d</sup>	2	<i>t</i> -C <sub>4</sub> H <sub>9</sub> -Br	63	2
CH <sub>2</sub> =CH <sub>2</sub>	167 <sup>e</sup>	5	C <sub>6</sub> H <sub>5</sub> -Br	71	4
CH <sub>3</sub> -CH <sub>3</sub>	88	2	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -Br	51	1
CH <sub>3</sub> -C <sub>2</sub> H <sub>5</sub>	85	2	CCl <sub>3</sub> -Br	54	2
CH <sub>3</sub> -CH(CH <sub>3</sub> ) <sub>2</sub>	83	2	CH <sub>3</sub> Cd-CH <sub>3</sub>	46	2
C <sub>2</sub> H <sub>5</sub> -C <sub>2</sub> H <sub>5</sub>	87	2	(CH <sub>3</sub> ) <sub>2</sub> In-CH <sub>3</sub>	47	2



TABLE XXXII (Continued)

Bond	$D_{298}$ , kcal	Estimated errors, kcal	Bond	$D_{298}$ , kcal	Estimated errors, kcal
$\text{CH}_3(\text{Cl}_2)\text{Sn}-\text{CH}_3$	56	?	HO-OH	51 <sup>a</sup>	1
$(\text{CH}_3)_2\text{Sb}-\text{CH}_3$	57	?	$\text{CH}_2\text{O}-\text{OH}$	43	3
$\text{CH}_3-\text{I}$	56.3	1	$\text{C}_2\text{H}_5\text{O}-\text{OH}$	43	3
$\text{C}_2\text{H}_5-\text{I}$	53.0	1	$n\text{-C}_2\text{H}_7\text{O}-\text{OH}$	44	3
$n\text{-C}_3\text{H}_7-\text{I}$	54	2	$t\text{-C}_4\text{H}_9\text{O}-\text{OH}$	44	3
$i\text{-C}_3\text{H}_7-\text{I}$	53	2	$\text{HCO}-\text{OCH}_3$	94	5
$t\text{-C}_4\text{H}_9-\text{I}$	50	2	$\text{CH}_3\text{O}-\text{OCH}_3$	36.1	1
$\text{C}_6\text{H}_5\text{CH}_2-\text{I}$	40	1	$\text{CH}_3\text{CO}-\text{OCH}_3$	97	5
$\text{CH}_3\text{CO}-\text{I}$	51	2	$\text{CH}_3\text{CO}-\text{OC}_2\text{H}_5$	96	5
$\text{CF}_3-\text{I}$	54	2	$\text{C}_2\text{H}_5\text{O}-\text{OC}_2\text{H}_5$	34.1	1
$\text{CH}_3\text{Hg}-\text{CH}_3$	50	2	$\text{CH}_3\text{CO}-\text{O}-n\text{-C}_4\text{H}_9$	98	5
$\text{C}_2\text{H}_5\text{Hg}-\text{C}_2\text{H}_5$	48	2	$\text{CH}_3\text{CO}-\text{O}-i\text{-C}_3\text{H}_7$	97	5
$\text{C}_2\text{H}_5\text{Hg}-\text{C}_2\text{H}_5$	43	2	$n\text{-C}_2\text{H}_7\text{O}-\text{OC}_2\text{H}_5$	36.5	1
$(\text{CH}_3)_2\text{Tl}-\text{CH}_3$	27	2	$\text{CH}_3\text{CO}-\text{O}-n\text{-C}_4\text{H}_9$	98	5
$(\text{CH}_3)_2\text{Bi}-\text{CH}_3$	44	2	$\text{CH}_3\text{CO}-\text{O}-i\text{-C}_3\text{H}_7$	99	5
$\text{NH}_2-\text{NH}_2$	56	2	$t\text{-C}_4\text{H}_9\text{O}-\text{OC}_2\text{H}_5$	37.4	1
$\text{NH}_2-\text{NHCH}_3$	52	2	$\text{C}_6\text{H}_5\text{CO}-\text{OCH}_3$	90	5
$\text{NH}_2-\text{N}(\text{CH}_3)_2$	50	2	$\text{C}_6\text{H}_5\text{CO}-\text{OC}_2\text{H}_5$	88	5
$\text{CH}_3\text{NH}-\text{NHCH}_3$	47	5	$\text{CH}_3\text{COO}-\text{OOCCH}_3$	30	2
$\text{CH}_3\text{NH}-\text{N}(\text{CH}_3)_2$	44	5	$\text{C}_2\text{H}_5\text{COO}-\text{OOC}_2\text{H}_5$	30	2
$(\text{CH}_3)_2\text{N}-\text{N}(\text{CH}_3)_2$	42	5	$n\text{-C}_2\text{H}_7\text{COO}-\text{OOC}_2\text{H}_5$	30	2
$\text{C}_6\text{H}_5\text{NH}-\text{NH}_2$	40	2	$\text{O}=\text{PF}_3$	130 <sup>h</sup>	5
$\text{C}_6\text{H}_5\text{NH}-\text{NHC}_6\text{H}_5$	22	?	$\text{O}=\text{PCl}_3$	122 <sup>h</sup>	5
$\text{ON}-\text{NO}_2$	9.5 <sup>f</sup>	0.5	$\text{O}=\text{PBr}_3$	119 <sup>h</sup>	5
$\text{O}_2\text{N}-\text{NO}_2$	12.9 <sup>g</sup>	0.5	HO-Cl	60 <sup>i</sup>	3
$\text{NF}_2-\text{NF}_2$	19.9	0.5	HO-Br	56 <sup>i</sup>	3
$\text{NF}_2-\text{F}$	58	5	HO-I	56 <sup>i</sup>	3

<sup>a</sup> Thermochemical from  $\Delta H_f^\circ(\text{OH}) = 9.3$ . <sup>b</sup> Electron impact (65). <sup>c</sup> Electron impact (59). <sup>d</sup> Thermochemical from  $\Delta H_f^\circ(\text{CH}) = 142$ . <sup>e</sup> Thermochemical from  $\Delta H_f^\circ(\text{CH}_2) = 90$ . <sup>f</sup> Equilibrium study (18). <sup>g</sup> Equilibrium study (70). <sup>h</sup> Heat of hydrolysis (44). <sup>i</sup> Heat of hydrolysis (68).

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