stereochemistry[3]). A much better yield resulted by treatment of the tetrahydropyranyl ether of allenic diol **7** (prepared from the tetrahydropyranyl ether of 2-hydroxy-2,6,6-trimethyl-cyclohexanone by reaction with the lithium derivative of but-3-yn-2-ol followed by reduction with lithium aluminium hydride) with the same acid yielded β-damascone (yield: 78%).

This facile transformation of allenic diol to β-damascone strongly suggests that natural damascenone is derived from allenic carotenoids (*e.g.* neoxanthin) through grasshopper ketone [6], allenic triol **9** and 3-hydroxy-β-damascone (**10**), and that β-damascone may be derived from deoxy-neoxanthin, which it is hoped to isolate in the near future.

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[3])   Prepared from 4-(2,6,6-trimethylcyclohex-1-enyl)-but-3-yn-2-ol acetate by epoxidation followed by lithium aluminium hydride reduction; NMR. (CDCl$_3$): 1.04(3H, *s*), 1.20(3H, *s*), 1.27(3H, *d*, *J* = 7Hz), 1.34(3H, *s*), 4,36(1H, *q*, *J* = 7 Hz), 5,46(1H, *d* × *d*, *J* = 7Hz, *J'* = 5Hz) ppm; IR. (liq.): 3350, 1955 cm^{-1}.

149. Homopolar– and Heteropolar Bond Dissociation Energies and Heats of Formation of Radicals and Ions in the Gas Phase. I. Data on Organic Molecules

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Summary. The literature data on heteropolar and homopolar 2-center bond dissociation energies in organic molecules in the gas phase and the corresponding heats of formation of radicals and ions have been critically evaluated. Data for more than 500 bonds are represented in tabular form together with the pertinent literature references.

Selected electron affinities and π-bond dissociation energies have also been incorporated. The follow-up paper will discuss some empirical general aspects of these data particularly regarding the effect of structure on the bond dissociation energies.

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I. Introduction

A. General. – The relationship between reactivity and structure of molecules or fragments of molecules constitutes one of the most challenging problems of general interest in chemistry. The knowledge of reliable specific bond dissociation energies, *i.e.* particularly the variation in bond strength with changes in structure contributes essential quantitative information to the reactivity-structure relationship.

In the last 20 years a number of reliable specific 2-center *homopolar* bond dissociation energies in molecules and radicals have bevome available, particularly as a result of kinetic measurements of reactions in the gas phase [1]–[6], using the iodine atom hydrogen abstraction technique developed and used by *Benson et al.* [4] which has proved to be a particularly useful tool. Parts of these data, relating to homopolar bond strengths have been reviewed previously by *Benson* [1] [2], *Benson &* *O'Neal* [3], *Golden & Benson* [4], *Kerr* [5], *Kerr & Trotman-Dickenson* [6] and others [7].

In contrast to the above very few defined *heteropolar* 2-center bond dissociation energies are known which is primarily due to the lack of thermodynamic data for gaseous anions. It is to be expected, however, that the improvements of the experimental methods (*e.g.* ion-cyclotron resonance, photodetachment, etc.) will lead to considerable growth in reliable data on gaseous negative ions during the next few years.

In this first paper the available data on *heteropolar* bond dissociation energies (D^*H°) and *homopolar* bond dissociation energies (DH°) are critically evaluated and summarized.

In a second paper, immediately following this one these data will be discussed in terms of 'substituent effects', 'stabilization energies in delocalized radicals' etc. and some empirical generalizations will be derived. Apart from its general use as a critical source of data and references it is hoped that the considerable and ever growing amount of information on bond dissociation energies will serve as a basis and inducement for theoretical considerations of chemical bonding capable of *quantitative* predictions.

B. Definition of bond dissociation energy. – Defining *standard specific bond dissociation energies* DH°_{298} (R–X) as the enthalpy change involved in breaking one mol of a particular bond R–X at 1 atmosphere pressure and 25° into two fragments one can write the thermodynamic relationship

$$RX \underset{-1}{\overset{1}{\rightleftarrows}} R^\cdot + X^\cdot \tag{1}$$

$$DH^\circ_{298} = \Delta H^\circ_{298}(1) = \Delta H^\circ_{f,298}(R^\cdot) + \Delta H^\circ_{f,298}(X^\cdot) - \Delta H^\circ_{f,298}(RX) \tag{A}$$

$$RX \underset{-2}{\overset{2}{\rightleftarrows}} R^+ + X^- \tag{2}$$
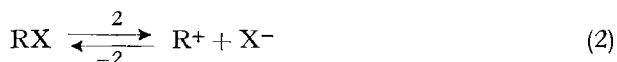
$$D^*H^\circ_{298} = \Delta H^\circ_{298}(2) = \Delta H^\circ_{f,298}(R^+) + \Delta H^\circ_{f,298}(X^-) - \Delta H^\circ_{f,298}(RX) \tag{B}$$

where $\Delta H^\circ_{298}(r)$ and $\Delta H^\circ_{f,298}$ represent standard heats of the reactions and heats of formation respectively.

Accurate data on bond dissociation energies are to be expected only if the nature of the R–X bond as well as that of the fragments are known. For gas phase systems,

the nature of the bond to be broken is in general well defined, compared to liquid phase. Particularly for heteropolar systems one is essentially limited to gas phase studies in order to avoid the inhibitive complications of unknown or ill defined, but often overruling solvent effects[2]).

The true structure of the fragments however, has only been established for very few relatively simple radicals or ions. In comparing data for different molecules, radicals or ions it should then be borne in mind, that the overall energetics observed in the bond breaking steps 1 or 2 may reflect different structures of the fragments rather than an inherent intrinsic bond property. This is particularly true for ions or radicals that allow electronic delocalization.

In agreement with the general definition given in equation 1, one can define a bond strength in ethylene as the heat of the reaction to form 2 CH_2-radicals. Except for specific areas like the very high temperature chemistry these data are of little practical use. Bond dissociation energies based on such 'thermodynamic' rather than 'kinetic' mechanistic considerations have not been incorporated into this review.

C. Scope. – This first part of the review is reserved for data concerning organic molecules. A second part will comprise the bond dissociation energies in inorganic and metalorganic molecules. It is also planned to review the experimental data on BDE's observed in radicals and ions at a later date. Only those data that could be properly evaluated both experimentally and on the basis of equation 1 or 2 have been considered. No claim can be made for an exhaustive coverage of the available information on BDE's, but all important categories of bonds for which BDE data are available have been listed in the tables. The data on sulfur and phosphorus containing molecules will be reported together with the organmetallic compounds.

D. Thermodynamic relationships and experimental methods. – The basic definitions have been given in equations A and B. The data listed in this review always refer to 25°, 1 atmosphere pressure and gas phase. From A and B the following relationship between homo- and heteropolar bond dissociation energies as defined in equations 1 and 2 can be derived:

$$DH^\circ_{298}(R–X) = D^*H^\circ_{298}(R–X) + \Delta H^\circ_i(R^\cdot) + \Delta H^\circ_i(X^\cdot) - \Delta H^\circ_i(R^+) - \Delta H^\circ_i(X^-) \quad (C)$$

This relationship also provides a check for the internal consistency of the data.

Most of the available data on homopolar bond dissociation energies and enthalpies of gaseous neutral radicals have been derived from kinetic measurements, *i.e.* from the activation energies E_1 for the bond breaking step in equation (1). Assuming that the activation energy E_{-1} for the reverse radical recombination step (– 1) be zero, it follows

$$\Delta H_{298}(1) = DH^\circ_{298}(R–X) = E_1 - E_{-1} \approx E_1. \quad (D)$$

The generalization of this assumption must be viewed with caution. For hexaethyl and hexacyclopropyl ethane E_{-1} appears to be in the order of 20 kcal mol^{-1} [9a].

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[2])   The fact that solvent effects can play a dominant role in determining relative bond strengths has recently been demonstrated with ion cyclotron resonance studies on gaseous R_3CO^- [7] and R_3N^- [8] anions. The relative intrinsic stabilities of these substituted anions in gas phase is reversed in liquid phase due to *solvent interaction*.

The recombination of t-butyl radicals has recently been observed to require an activation energy of 4.7 kcal mol^{-1} [9b] compared to 0 for methyl-radical and ethyl-radical recombination [9c] and a value of ∼2.5 kcal mol^{-1} for recombining methyl with t-butyl radicals. These data need further substantiation before they can be rigorously applied, and all the homopolar bond dissociation energies listed in this review have therefore still been based on the assumption $E_{-1} = 0$ and no allowance for a possible steric effect in the case of the t-butyl type structures was made.

One of the most important advantages of the kinetic methods, namely that of selective reactivity of the various bonds in a molecule constitutes also one of the most serious limitations of the method: accurate values for DH^0 can usually only be obtained for the weakest R–X bond (with respect to a particular reaction) in the molecule.

Direct measurements of the activation energies involved in breaking a bond *heterolytically* into ions are made impossible by the fact, that the thermally induced homopolar bond breakage requires much less energy. It is then necessary to determine the heats of formation of the positive and negative ions individually *via* ionization or appearance potential and electron affinity.

The *Ionization Potential* (IP) is given by

$$R^{\cdot} \underset{-3}{\overset{3}{\rightleftharpoons}} R^+ + e^- \tag{3}$$

$$IP = \Delta H^{\circ}(3) = \Delta H^{\circ}_{f,\,298}(R^+) - \Delta H^{\circ}_{f,\,298}(R^{\cdot}) \tag{E}$$

The *Appearance Potential* (AP) relates to

$$RX + e^- \underset{-4}{\overset{4}{\rightleftharpoons}} R^+ + X^{\cdot} \tag{4}$$
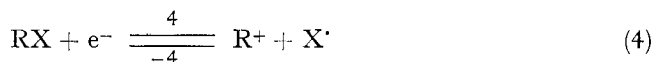
$$AP_{298}(R^+) = \Delta H^{\circ}_{298}(4) = \Delta H^{\circ}_{f,\,298}(R^+) + \Delta H^{\circ}_{f,\,298}(X^{\cdot}) - \Delta H^{\circ}_{f,\,298}(RX)$$

Combining 3) and 4) results in

$$D^*H^{\circ}_{298}(R–X) = AP_{298}(R^+) - IP_{298}(R^{\cdot}) \tag{F}$$

Considering the relatively large experimental uncertainties usually attached to both AP and IP, *homopolar* bond dissociation energies derived from mass spectrometric data are usually much less reliable than 'kinetic' data. Furthermore special attention must be given the problem of producing fragments carrying excess energy.
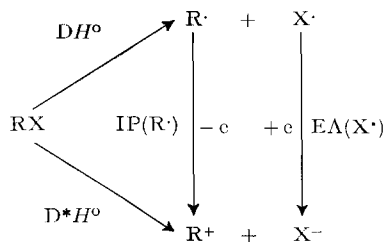
The *Electron Affinity* (EA) is given by:

$$e^- + X^{\cdot} \underset{-5}{\overset{5}{\rightleftharpoons}} X^- \tag{5}$$

$$- EA = \Delta H^{\circ}_{298}(5) = \Delta H^{\circ}_{f,\,298}(X^-) - \Delta H^{\circ}_{f,\,298}(X^{\cdot})$$

$$\text{with} \quad \Delta H^{\circ}_{f}(e^-) = 0$$

Combining A–G results in the relationship

$$DH^\circ(RX) - EA(X^\cdot) + IP(R^\cdot) - D^*H^\circ(RX) = 0 \tag{H}$$

Whenever possible the data on heats of formation of carbonium ions listed in the tables have been derived from photoionization (PI) or electron impact (EI) measurements which usually yield the most reliable data on $\Delta H_f^\circ(R^+)$. For an account of the various methods and estimated reliabilities used to obtain $\Delta H_f^\circ(R^+)$ compare references [10]–[12] and the original literature cited therein.

Quantitative information on the minimum energy required to detach an electron from an atom, radical or molecule, *i.e.* the *electron affinity* have been deduced from measurements based on a variety of methods [11] [12] *e.g.* photodetachment [13], electron impact [14], photodissociation [15], surface ionization [16], kinetic energies of ions, kinetics of ion-molecule reactions etc. The extremely large scatter of the data reported [12] demonstrate the problems related with determinations of electron affinities. Data on *reliable* gas phase electron affinities have so far been limited to atoms and small molecules, whereby primarily photodetachment and electron impact methods were used. The method of studying photodetachments of electrons from negative ions using the ion cyclotron resonance spectrometer developed in recent years [7] [8] [17]–[20] promises to supply a number of electron affinities for larger gaseous ions, not accessible by previous methods. Ion cyclotron resonance spectroscopy has also been shown to provide a very powerful tool in determining relative acidities and basicities of gaseous ions [8] [19]–[22] by studying ion-molecule reactions. From these measurements limiting values for electron affinities can be derived. Similar studies of negative ion-molecule reactions have been carried out using a flowing afterglow technique [23–28].

II. Bond dissociation energies

A. Origin of heats of formation. – 1) *Molecules.* The heats of formation for the gaseous molecules at 298 K and 1 atmosphere pressure, $\Delta H_{f,298}^\circ$, have been taken from *Cox & Pilcher* [29], or *Stull, Westrum & Sinke* [30]. Other sources of experimental data have been individually referenced. Where no experimental data have been available, but incorporation of data was considered important, $\Delta H_{f,298}^\circ$, values have been estimated on the basis of the incremental 'group' additivity method [31].

2) *Radicals.* The values for $\Delta H_{f,298}^\circ$ of radicals have been critically selected based on the data given in one of the following pertinent reviews: *Kerr & Trotman-Dickenson* [6], *Golden & Benson* [4], CODATA Key values [32], JANAF Thermochemical Tables [33]. Other sources have been individually referenced. As mentioned previous-

ly, practically all $\Delta H^\circ_{f,298}(R^\cdot)$ data except those for the inorganic atoms and radicals have been obtained from kinetic studies in the gas phase, whereby unimolecular thermal decompositions or reactions induced by iodine or bromine atoms [4] have contributed the bulk of the data. Both static and flow techniques have been used to determine the activation energies of the various processes which are then related to the corresponding bond dissociation energies. Accounts of these various methods, their reliabilities and the expected experimental error limits habe been given in a variety of physical chemistry and kinetic texts [2] [3] [34]–[35]. The data for $\Delta H^\circ_f(R^\cdot)$ and $\Delta H^\circ_f(X^\cdot)$ have been corrected for temperature where necessary.

3) *Ions.* All the data listed in the tables refer to 298 K and 1 atm. and are given in units of kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ). As the temperature effect (where known) for heats of formations of *ions* does not appear to be larger than for radicals all reported ionization and appearance potentials as well as electron affinities can

Table 1. *Selected electron affinities and preferred heats of formation of negative ions*

X	EA(X) eV [a]	$\Delta H^\circ_{f,298}[X^-]$ kcal mol^{-1}	References
H	0.756	34.7	[11]
OH	1.83±0.04	− 33.2	[18] [19]
OCH$_3$	≳1.4	≳ − 30	[b]
NH$_2$	0.744 ±0.02	30.0	[18] [19] [36]
F	3.40 ±0.02	− 60	[11]
Cl	3.61 ±0.03	− 54.3	[11]
Br	3.36 ±0.03	− 50.9	[11]
I	3.06 ±0.03	− 45.1	[11]
NO	0.024 ±0.01	21	[37]
NO$_2$	2.38 ±0.06	− 47	[25]
NO$_3$	3.9 ±0.2	− 73.3	[24]
Cl$_2$	2.46 ±0.14	− 56.7	[25]
H$_3$Si		(7–16) [c]	[18] [19]
H$_2$P	1.25 ±0.03	0.4	[36]
H$_2$As	1.27 ±0.03	[d]	[38]
HS	2.32 ±0.01	− 20.5	[36] [38] [39]
HSe	2.21 ±0.03		[21]
C$_6$H$_5$	1.2–1.6	41–50	[27]
C$_6$H$_5$CH$_2$	0.4–0.9	(>35)	[27]
	≳0.39		[8]
CH$_3$	∼0	(∼34)	[e]
n-C$_3$H$_7$	≲EA(O$_2$) ≲ 0.440		[28]

[a]   1 eV = 23.0609 kcal mol^{-1}.

[b]   Based on EA(C$_2$H$_5$Ȯ) − EA(C$_6$H$_5$ĊH$_2$) ≈ 19 kcal mol^{-1} and on the low limit value of EA(C$_6$H$_5$ĊH$_2$) ≳ 9 kcal mol^{-1} yielding EA(C$_2$H$_5$Ȯ) ≳ 28 kcal mol^{-1} [21] [8]. Considering that the DH°(CH$_3$O—H) ≈ DH°(CH$_3$CH$_2$O—H and EA generally increases with increasing size of the alkyl group, EA (CH$_3$Ȯ) can be estimated at ≳ 32. This value is in good agreement with the limiting values obtained by *Bohme et al.* [26] and also with earlier data of *Williams & Hamill* [40].

[c]   Based on a H$_3$Si—H bond dissociation energy of 80 kcal mol^{-1} [18] [19] [36].

[d]   The heats of formation of the corresponding radicals are not available.

[e]   Estimated value based on the relative acidities observed by *Brauman et al.*, using icr studies [36]. An upper limit value of about 10 kcal can be estimated for EA(CH$_3$).

be treated as heats of reaction at 298 K, introducing at worst an error of ~ 1.5 kcal mol^{-1}. At this time it would be impractical and in most cases impossible to apply proper temperature corrections to the data for $\Delta H_f^o(R^+)$ and $\Delta H_f^o(X^-)$.

The heats of formation of the *positive gaseous ions* have been calculated on the basis of the data given in the critical review of *Franklin et al.* [10], corrected for the latest ΔH_f^o-values for the corresponding radicals. The heats of formation of the *negative gaseous ions* have been calculated from the heats of formation of the corresponding radicals and the selected 'preferred' electron affinities given in Table 1.

Unless otherwise referenced, the data have been based on the values given in the compilations of *Berry* [11], *Beauchamp* [20], or *Pritchard* [41]. Data considered to be uncertain by more than ± 0.3 eV (7 kcal mol^{-1}) have not been taken into account in making up the key tables. As can be seen from table 1, reliable data on electron affinities of molecules and radicals in the gas phase is still very sparse, particularly for polyatomics. This fact then limits the available data for heteropolar bond dissociation energies drastically, compared to the values for homopolar bond breakage. For further compilations of electron affinities and ionization potentials compare also *Page & Goode* [16] or *Blaustein & Christophorou* [12].

B. Accuracy of the data. – It is evident, that the accuracy of the data listed in the tables may vary considerably between relatively simple and well investigated structures and more 'exotic' bonds. At the outset of this work estimates of the individual error limits had been incorporated in the tables, but it became apparent, that this would unduly complicate both the presentation and the legibility of the data.

The confidence limits of the data can be estimated however from the general guidelines observed in setting up the tables:
– Unreliable values have not been incorporated.
– Values with larger uncertainties than 'average' are shown in parentheses.
– Where additional but clearly defined assumptions were necessary to generate the data, this is indicated and discussed in footnotes, but in this case the data have *not* been bracketed even though the overall uncertainty (including the additional assumption) might exceed average error limits.

For the *homopolar bond dissociation energies* 'average' error limits in terms of standard deviations originating from experimental errors and defined assumptions (but disregarding possible systematic errors of the method) amount to $\sim \pm 1.5$ kcal mol^{-1}. For hydrocarbon and related molecules a value of 1.5 kcal mol^{-1} or less also constitutes the confidence limit, that can be attached to these data. For complicated radical structures, *e.g.* cyclo-$C_5H_5\cdot$ or $HCCH_2\cdot$, the values for the heats of formation
$$\overset{\parallel}{O}$$
of these radicals are much less well established, encompassing possible methodical error limits of 5 kcal mol^{-1} even though the observed experimental error limits may be considerably lower.

The error limits attached to the data for *heteropolar* BDE are in general much larger and sometimes very difficult to assess. The best experimental technique yield values for the heats of formation of negative or positive ions within ± 1.5 kcal mol^{-1}. For most data the uncertainties are considerably larger however. 'Average' error limits for reliable D^*H^o-data can be assumed to be ± 3 to 5 kcal mol^{-1}. Confidence limits on an absolute basis are likely to amount to ± 5 to 10 kcal mol^{-1}, however.

C. R-X Bond dissociation energies. – Bond dissociation energies $DH^{\circ}_{298}(R-X)$ and $D^{*}H^{\circ}_{298}(R-X)$ together with the corresponding heats of formation of radicals R and $X^{\cdot}$ and ions R^{+} and X^{-} are presented in the four key blocktables 2–4. In *Table 2* are summarized data on R–X bonds where R represents hydrogen alkyl- or cycloalkyl groups. *Table 3* gives data for R–X bonds where R represents unsaturated olefinic or aromatic groups. *Table 4* comprises those R–X bonds where R contains oxygen and *Table 5* where R contains halogen atoms.

All data are given in kcal mol^{-1} and refer to 'standard' gas phase conditions, *i.e.* 25°, 1 atmosphere of pressure. The nomenclature is based on the definitions of $DH^{\circ}_{298}(R-X)$ given in equations A and B respectively.

For reasons of simplicity in the notation, bonded hydrogens have usually been omitted in marking R in the vertical leading columns of the table 2–5.

Homopolar bond dissociation energies DH° and the corresponding heats of formation of the radicals are shown in the upper entries of the blocks and in fatter print.

Heteropolar bond dissociation energies $D^{*}H^{\circ}$ and the corresponding heats of formation of the ions are shown as lower entries of the blocks and in regular print. Heats of formation, $\Delta H^{\circ}_{f,298}(R^{\cdot})$ and $\Delta H^{\circ}_{f,298}(R^{+})$, are represented accordingly with upper and lower entries respectively in the vertical leading column for $R^{\cdot}$. In the horizontal leading column for X, $\Delta H^{\circ}_{f,298}(X^{\cdot})$ is shown above and $\Delta H^{\circ}_{f,298}(X^{-})$ below the symbol for X.

In setting up these tables particular care was taken to avoid built-in artificial pseudo-consistencies by using original data whenever possible. The only *estimated* values that have entered the tables are those for heats of formation of molecules in cases where no literature data were available. The incremental group additivity method used in estimating these data has been shown to be very reliable [31].

D. Use of the key tables. – It was not possible to incorporate all the data of a homologous series of molecules in the key tables 2 to 5. If a particular bond is missing in the tables, one should then first look for homologous or related compounds.

With few exceptions, discussed in the follow-up paper, substituents that are not directly bonded to one of the reactive center involved in bond breaking usually have negligible effects on the bond strength, when compared with the experimental uncertainties of the data. The homopolar primary C–H bond dissociation energy as an example is the same in ethane, propane, butane, ... etc. and similar observations have been made for other bonds in homologous series of compounds such as alkyl O–H compounds [1]. The use of the tables is exemplified below with three examples.

a) *i-propylchloride:* The homopolar DH° (C–Cl) is 80.4 kcal mol^{-1} compared to 170 kcal mol^{-1} for the heteropolar $D^{*}H^{\circ}$. The heats of formation of the fragments (in kcal mol^{-1}) are 17.8 for the *i*-propyl radical, 29.0 for the chlorine atom, 191 for the *i-propyl* cation and – 54.3 for the chlorine anion.

b) *Isopropyl-methylether.* The only homopolar DH° of this structure that can be taken directly from table 4 is that for bond 3 (81.4 kcal mol^{-1}).
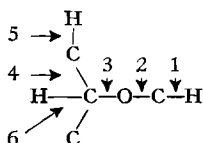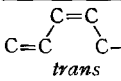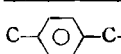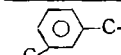
Table 2. *Homopolar and heteropolar R—X bond dissociation*

$\Delta H^0_f(\dot{R})$ / R—X / $\Delta H^0_f(R^+)$ $\quad$ $\Delta H^0_f(\dot{X})$ / $\Delta H^0_f(X^-)$	52.1 H 34.7	34.0 CH$_3$ (~34)	25.7 C$_2$H$_5$	20.8 n-C$_3$H$_7$	17.8 i-C$_3$H$_7$	7.5 t-C$_4$H$_9$	18.9 F −60
H— $\quad$ 52.1 / 366	104.2 / 401	104 / (418)	98	98	95	92	135.8 / 370
CH$_3$ $\quad$ 34 / 260	104 / 313	88.2 / (315)	84.8	85.2	84.2	81.8	108.8[f] / 256
C$_2$H$_5$— $\quad$ 25.7 / 219	98 / 274	84.8 / (278)	81.8	81.6	80.4	77.9	107.1[f] / 220
n-C$_3$H$_7$— $\quad$ 20.8 / 208	98 / 268	85.2 / (273)	81.6	81.5	80.4	77.5	107.3 / 214
i-C$_3$H$_7$— $\quad$ 17.8 / 191	95 / 251	84.2 / (258)	80.4	80.4	78.2	74.2	106.1 / 200
t-C$_4$H$_9$— $\quad$ 7.5 / 167	92 / 234	81.8 / (242)	77.7	77.5	74.2	68.8	108.4[f] / 189
▷— $\quad$ 61.3[c] / 239	100.7 / 261	89.6[e] / (268)	86.2[e]	86.3[e]	85.4[e]	82.7[e]	110.9[e] / 210
◇— $\quad$ 51.2[c],[z] / 214	96.5 / 242	85.8[e] / (249)	82.5[e]	82.5[e]	81.6[e]	79[e]	107.2[e] / 191
⬠— $\quad$ 24.3[d] / 193	94.8 / 246	83.6 / (253)	80.3	80.5	79.6[e]	77[e]	105.2[e] / 195
⬡— $\quad$ 13.9[c] / 185	95.5 / 249	84.9 / (256)	80.6	80.9	80.4[e]	77.8[e]	106[e] / 198
⬢— $\quad$ 12.2[e]	92.5	81.5[e]	78.2[e]	78.2[e]	77.3[e]	74.7[e]	102.9[e]

energies (in kcal mol⁻¹). H—X, Alkyl—X, Cycloalkyl—X Bonds.

Cl	Br	I	OH	OCH₃	NH₂	NHCH₃	N(CH₃)₂	NO	NO₂
29.0	**26.7**	**25.5**	**9.0**	**3.4**[a]	**47.2**[b]	**45.2**[b]	**38.2**[b]	**21.6**	**7.9**
−54.3	−50.9	−45.1	−33.2	(≳ −30)	30			(21)	(−47)
103.1	**87.4**	**71.3**	**119**	**105**	**110**	**103**	**95**	**49**	**79**
334	324	315	390	(386)	407			(412)	(336)
83.6	**69.8**	**56.1**	**91.1**	**81.4**	**86.7**	**83.6**	**77.9**	**40**[g]	**60**
227	219	212	274	(274)	296			(265)	(230)
80.8	**67.6**	**53.2**	**90.9**	**80.8**	**84.3**	**82.3**	**76.3**[e]	**(38)**[h]	**58**
191	184	176	242	(241)	261			(231)	(196)
80.1	**68.0**	**53.4**	**91.0**	**81.0**	**84.8**	**82.3**[e]	**76.4**[e]	**(38)**[h]	**59**
185	178	171	235	(236)	255			(225)[h]	(190)
80.4	**68**	**53.1**	**91.9**	**81.4**	**85**	**83**[e]	**77.1**[e]	**37**[g]	**59**
170	164	156	222	(221)	241			(210)	(177)
80.2	**66.1**	**50.4**	**91.2**	**80.6**	**83.6**	**80.8**[e]	**74.9**[e]	**36**[g]	**(58)**[h]
157	149	140	208	207	226			(195)	(162)
85.4[e]	**73.7**[e]	**58.6**[e]	**97.5**[e]	**87.8**[e]	**91.2**[e]	**88.7**[e]	**82.8**[e]	**(42.7)**[h]	**67.3**[e]
180	174	166	233	232	252			(220)	(192)
81.7[e]	**69.9**[e]	**54.9**[e]	**93.7**[e]	**84**[e]	**87.4**[e]	**84.9**[e]	**79**[e]	**(38.9)**[h]	**63.6**[e]
161	155	147	214	213	233			(201)	(171)
79.7[e]	**67.9**[e]	**52.9**[e]	**91.3**	**82**[e]	**85.4**[e]	**82.9**[e]	**77**[e]	**(36.2)**[h]	**61.5**[e]
165	159	151	218	217	237			(207)	(175)
82	**68.7**[e]	**51.6**	**91.3**	**82.8**[e]	**86.2**[e]	**83.7**[e]	**77.8**[e]	**(37)**[h]	**(62.4)**[e]
170	162	153	215	220	240			(210)	(178)
77.4[e]	**65.6**[e]	**50.6**[e]	**89.4**[e]	**79.7**[e]	**83.1**[e]	**80.6**[e]	**74.7**[e]	**(37)**[h]	**59.2**[e]

Table 3. *Homopolar and heteropolar R—X bond dissociation energies* (in kcal

$\Delta H_f^\circ(\dot{R})$ / R—X / $\Delta H_f^\circ(R^+)$	$\Delta H_f^\circ(\dot{X})$ / $\Delta H_f^\circ(X^-)$	52.1 / H / 34.7	34 / CH$_3$ / (~34)	25.7 / C$_2$H$_5$	20.8 / n-C$_3$H$_7$	17.8 / i-C$_3$H$_7$	7.5 / t-C$_4$H$_9$	18.9 / F / −60
C=C—	68.4	108	97.5	94.3	94.5	92.8	90.4	118.7
	269	291	(293)					240
C$_6$H$_5$— (⟨O⟩—)	77.7[k]	110	99.7	96.3	96.6	94.5	90.6	123.9
	285	300	(308)					253
C=C—C—	41.4	88.6	75.6	72.4	72.2	71.5	68.3	97.7[m]
	226[l]	256	(261)					203[n]
C=C—C— (with C branch)	30.4	82.5	71.0	67.9	67.2[f]	65.8[f]	64.4[e]	93.5[m]
	203	238	(244)					187[n]
(ring structure)	38.4[o]	82.3	71.6[m]	67.8[m]	67.2[m]	65.6[m]	61.6[m]	93.5[m]
C≡C—C—	86.2[p]	93.9	81.1[m]	77.5[m]	77.4[m]	76.3[m]	73.4[m]	103.2[m]
	254	244	249[n]					192[n]
C=C⟍ / C=C / C—	48.3	75.2	64.2[m]	60.4[m]	60.4[m]	58.2[m]	54.2[m]	86.1[m]
C=C / C⟍ C— *trans*	48.3	82.3	69.5[m]	65.9[m]	65.8[m]	64.7[m]	61.8[m]	91.6[m]
(ring structure)	(55[r])	(75.2)[r]	(64.2)[m]	(60.4)[m]	(60.4)[m]	(58.2)[m]	(54.2)[m]	(86.1)[m]
	273[q]	275	(283)					225
(cyclohexadiene)	44[s]	69.8	59[m]	55.2[m]	55.2[m]	53[m]	49[m]	80.9[m]
(cyclohexadiene)	44[s]	70.1	59.3[m]	55.5[m]	55.5[m]	53.3[m]	49.3[m]	81.2[m]
(cycloheptatriene)	65[x]	73.2	61.2[e]	57.9[e]	57.9[c]	57[e]	54.4[e]	81.9[m]
	209[x]	200	205[e]					147[m]
⟨O⟩—C—	44.9	85	71.8	68.7	69	67.8	65[e]	96.3[e]
	224	247	(251)					196
C—⟨O⟩—C—	37[v]	84.8	71.8	68.4[e]	68.4[e]	67.6[e]	65[e]	95.1[w]
	209	240	(244)					188
⟨O⟩—C— (with C)	37[v]	85	71.4	68.5	68.4	67.6	65	95.1[w]
	213	244	(248)					192

Footnotes to Tables 2 and 3

a) Ref. [3]; b) Ref. [42]; c) Ref. [43]; d) Ref. [44]; e) The heats of formation of the molecules
h) Interpolated value; i) Including substituted R—X bonds. For further information on the origin
responding bond in the parent alkane, reduced by the stabilization energy produced in the R˙ –
q) Ref. [50]; r) An upper limit for 'stabilization energy' E_s in the cyclopentadienyl radical of 20 kcal
$\Delta H^\circ_f[C(C)(N)(H_2)] \approx -6.6$ kcal mol^{-1}, $C(C_B)(NO)(H_2) \approx C(C)(NO)(H_2) \approx 19.1$ and $C(C_B)(NO_2)(H_2)$
corrections; w) $\Delta H^\circ_f C(C_B)(Cl)(H_2) \approx -17.1$, $\Delta H^\circ_f C(C_B)(F)(H_2) \approx -53.3$, $\Delta H^\circ_f C(C)(Cl)(H_2) \approx$

mol⁻¹). Vinyl —X, Allyl —X, Benzyl —X and Phenyl —X type bonds[1]

| 29	26.7	25.5	9.0	3.4	47.2	45.2	38.2	21.6	7.9
Cl	Br	I	OH	OCH_3	NH_2	$NHCH_3$	$N(CH_3)_2$	NO	NO_2
− 54.3	− 50.9	− 45.1	− 33.2	(≳ − 30)	30			(21)	(−47)
88.8	76.4	63 [e]	100.4 [e]	88.2 [e]					
207	200	194	259 [n]	255					
94.5	79.2	64.4	109.7	98.4	104.1				
219	210	202	275	272	294				
71.2 [m]	57.2	44.1	80	70.3 [e]	75.2 [m]	72.7 [m]	66.8 [m]	(28) [m]	49.4 [m]
173 [n]	165	159	223	222	243 [n]			212 [n]	179 [n]
67.8 [m]	55.4 [m]	40.5 [m]	79.3 [m]	68.8 [m]	72.4 [m]	70.4 [m]	64.5 [m]	24 [m]	46 [m]
158 [n]	151 [n]	143 [n]	210 [n]	208 [n]	228 [n]			196 [n]	164 [n]
67.8 [m]	55.4 [m]	40.5 [m]	79.3 [m]	68.8 [m]	72.4 [m]	70.4 [m]	64.5 [m]	(23.6) [m]	48.9 [m]
76.7 [m]	63.9 [m]	49.3 [m]	86.9 [m]	76.9 [m]	80.7 [m]	78.2 [m]	72.3 [m]	(33.9) [m]	54.9 [m]
161 [n]	154 [n]	147 [n]	213 [n]	211 [n]	231 [n]			201 [n]	168 [n]
60.4 [m]	48 [m]	33.1 [m]	71.9 [m]	61.4 [m]	65 [m]	63 [m]	57.1 [m]	(17) [m]	39 [m]
65.1 [m]	52.3 [m]	37.7 [m]	75.3 [m]	65.3 [m]	69.1 [m]	66.6 [m]	60.7 [m]		
60.4) [m]	(48.0) [m]	(33.1) [m]	(71.9) [m]	(61.4) [m]	(65) [m]	(63) [m]	(57.1) [m]		
196	189								
55.2 [m]	42.8 [m]	27.9 [m]	66.7 [m]	56.2 [m]	59.8 [m]	57.8 [m]	51.9 [m]	(12.4) [m]	37.8 [m]
55.5 [m]	43.1 [m]	28.2 [m]	67 [m]	56.5 [m]	60.1 [m]	58.1 [m]	52.2 [m]		
66.4 [m]	44.6 [m]	29.6 [m]	68.4 [m]	58.7 [m]	62.1 [m]	59.6 [m]	53.7 [m]	(16) [m]	38.2 [m]
121 [m]	111 [m]	102 [m]	170 [m]	169 [m]	189 [m]	188 [m]		159 [m]	127 [m]
69.4	54.7	40 [t]	77.9	66.9 [e]	71.9 [u]			25 [u]	45.9 [u]
166	157	149	215	212	236			(206)	(170)
69 [w]	56.5	40	76.3	66.6	71.9 [u]			25	45.9
158	152	142	206	205	229			(197)	(162)
69 [w]	56.5	40	76.3	66.6	71.9 [u]			25	45.9
162	156	146	210	207	233			(201)	(166)

calculated from incremental 'group' additivity method outlined in ref. [31];   [f] Ref. [30];   [g] Ref. [45];
of the data compare Table 2;   [k] Ref. [46];   [l] Ref. [47];   [m] Calculated from the $DH°$ of the cor-
radical (compare Table 8);   [n] $\Delta H°_f$ of the molecules calculated from $DH°$;   [o] Ref. [48];   [p] Ref. [49];
mol⁻¹ has been used (compare Table 8);   [s] Ref. [51];   [t] Ref. [52];   [u] $\Delta H°_f[C(C_B)(N)(H_2)] \approx$
$\approx C(C)(NO_2)(H_2) \approx -15.1$ assigned;   [v] $\Delta H°_f$(radical) calculated from ⟨O⟩—CH_2 using 'group'
− 1.5;   [x] Ref. [53];   [y] Ref. [90];   [z] Ref. [91].

Table 4. *Homopolar and heteropolar R—X bond*

$\Delta H_f^o(\dot{R})$ / R—X / $\Delta H_f^o(R^+)$	$\Delta H_f^o(\dot{X})$ / $\Delta H_f^o(X^-)$	52.1 H 34.7	34 CH_3 (~34)	25.7 C_2H_5	20.8 $n\text{-}C_3H_7$	17.8 $i\text{-}C_3H_7$	7.5 $t\text{-}C_4H_9$
O=C—	9.5 / 204 c)	87.5 / 265	83.2 / (278)	80.7	79.2	79.6	75.2 g)
O=C— / C	−5.8 d) e) / 152	86 / 227	80.1 / (232)	76.9	76.9	74.8	71
O=C— / ⟨phenyl⟩	26.1 / (191)	86.9 / 235	80.8 / (246)	77.8	77.5	77.3 g)	73.6 g)
O=C—C— / C	(−5.5) h) / 143	(98.5) i) k) / 230	(85.5) i) k) / (235)	(82.1) i) k)	(82.2) i) k)	(80.9) i) k)	(78.3) i) k)
HO—C—	−4.6 / 174 q)	95.6 r) / 257	85.6 / (265)	82.3	82	81	76.3 g)
C / HO—C— / C	−27.1 / (156)	90.1 t) / 257	81.6 / (265)	77.7			
O=C— / OH	−52.7 / 189	90 q) / 315	84.6 / (327)	81.4	80.5	80.8 g)	77.3 g)
O=C— / OCH_3	−40.4 v)	95.3 b) / (92.6 v)	91.5 b)	88.2 g)	88.2 g)	89.6	89.9
O=C—O— / C	−45 w)	110.4	86.9 b)	87	87 g)	87.9	87.1 g)
⟨phenyl⟩—O—	9.9 / 226	85 / 284	61.2 / (278)	61.9	62.1 g)	62.8 g)	62.1 g)
CH_3O—	3.4 / 202 q)	103.6 r) / 285	81.4 / (281)	80.8	81	81.4	80.6
C—O—C—	−2.8 j) / (163)	93.3 j) / (243)	82.9 / (249)	79.7	80.3 g)	79.3 g)	76.7 g)

a) ΔH^o_f of the molecule calculated on the basis of ΔH^o_f for acetylhalides, adding an incremental
c) Ref. [54]; d), Ref. [55]; e) Ref. [56]; f) Ref. [57]; g) ΔH^o_f of the molecule calculated using the
[58]; i) Ref. [59]; j) Ref. [60]; k) Stabilization energy (E_s) for O=C—C· taken as O±1 kcal mol⁻¹
be 1±1 kcal mol⁻¹. Small ring pyrolysis data however suggest a stabilization energy of 7.6±1
estimated based on $C(C)(H_2)(X)$ and $\Delta[C(C)(H_2)(Br)]\text{-}[C(CO)(H_2)(Br)]$; m) Ref. [61]; n) Based on
r) Ref. [64]; s) ΔH^o_f groups estimated from $C(F)(C_2)(O) \approx C(F)(H_2)(O) \approx -56$, $C(Cl)(C_2)(O) \approx$
3.8 m; t) Ref. [65]; u) Ref. [1]; v) Ref. [66]; w) Ref. [5]; x) $\Delta H^o_f O(C_B)(O)=\Delta H^o_f O(C)(O) = -4.5$
average difference between $\Delta H^o_f CH_3O$—X and C_6H_5C—X; z) Ref. [67].

dissociation energies (in kcal mol^{-1}). *R containing oxygen*

18.9	29	26.7	25.5	9.0	3.4	47.2	45.2	21.6	7.9
F	Cl	Br	I	OH	OCH$_3$	NH$_2$	NHCH$_3$	NO	NO$_2$
−60	−54.3	−50.9	−45.1	−33.2	(≳ −30)	30		(21)	(−47)
(122)[a]	(84)[a]	(69)[a]	(52)[a]	109.1	96.1[b]	101.2[b]	98.8[g]		
(237)[a]	(196)[a]	(187)[a]	(177)[a]	262	258[b]	279[b]			
119.5	81.6	66.5	49.8	106.5	95.5[b]	99.2[g]	96.8[g]		
198	157	147	138	223	220[b]	240			
(115)[g]	80.5[f]	64.4	49.1	105.2	95.1[g]	94.8[g]	92.4[g]		
200	162	152	144	228	235	243			
(102)[k][l]	(77)[k][l]	(64.2)[h-m]	(50.2)[k][n]	(89.9)[k][p]	(80.2)[k][p]				
171	142	136	128	197	193				
(101)[s][g]	(82.2)[s][g]	(69.7)[s][g]	(55.1)[s][g]	97.9[g]	88.2				
205	183	177	169	235	231				
(106)[s][g]	(80)[s][g]	(67)[s][g]	(53)[s][g]	94.6[g]	84[g]				
207	182	173	166	236	234				
				42.8[g]	38.5[g]				
				25[x]	17.7	(38.5)[g]	(39.1)[g]	23.7[y]	21.2[y]
				199	200	238			
				44[z]	36.9	(56.8)[g]	57.4[g]	42.9	40.4
				201	200	240		(241)	(186)
(106)[s][g]	(79.9)[s][g]	(67.4)[s][g]	52[m]	95.6[g]	83.9				
192	163	156	149	220	216				

value of 12.7 kcal mol^{-1} derived from formic acid/acetic acid; [b]) See footnote f to Tables 2 and 3; principle of group additivity outlined in Ref. [31] and the data listed in Ref. [29] and [74]; [h]) Ref. as obtained by the iodine atom abstraction method (Ref. [4]), whereby E_a for HI + R$^{\cdot}$ is assumed to kcal mol^{-1} in which case the D$H°$ values should be lowered by ∼8 kcal mol^{-1}.   [l]) $\Delta H°_f$ groups $\Delta H°_f$ of 2-iodo-3-butanone; [o]) Ref. [62]; [p]) $C(CO)(O)(H_2) = C(C_d)(O)(H_2)$ assigned; [q]) Ref. [63]; $C(Cl)(H_2)(O) \approx -19.8$, $C(Br)(C_2)(O) \approx C(Br)(H_2)(O) \approx -9.6$ and $C(I)(C_2)(O) \approx C(I)(H_2)(O) \approx$ kcal mol^{-1} assigned; [y]) Calculated from CH$_3$O-derivatives −19.2 kcal mol^{-1} (±0.7) observed for

Table 5. *Homopolar and heteropolar R—X bond dissociation energies* (in kcal mol^{-1}) *R containing halogen*

$\Delta H_f^o(\dot{R})$ \ $\Delta H_f^o(\dot{X})$		52.1	34	25.7	20.8	18.9	29	26.7	25.5	9.0	3.4
R—X $\quad \Delta H_f^o$		H	CH$_3$	C$_2$H$_5$	n-C$_3$H$_7$	F	Cl	Br	I	OH	OCH$_3$
$\Delta H_f^o(R^+)$ \ (X$^-$)		34.7	(~34)			−60	−54.3	−50.9	−45.1	−33.2	(≳ −30)
CH$_2$F—	(≳ −5.3)[a]	102.7 [b]	91.2 [b]	88	87.3	122	(89)[c]	(73)[c]		(97.6)[d]	(87.5)[d]
	209	301	(300)			319	277	262		270	269
CHF$_2$—	(≳ −57)[a]	103.2	95.8	93 [e]	93 [e]	128	87.6	(70)[c]			
	143	286	(296)			311	261	245			
CF$_3$—	−112.5[a]	105.9	99.5	(96.6)[f]	(96.7)[f]	129.7	85.5	69.2	53.6		
	(101)[m]	(302)	(314)			(264)	(216)	(206)	(197)		
CH$_2$Cl—	29[a)[g]	101.7	89.1	85.7	84.9	(113)[c]	81	(65)[c]		(95.7)[d]	(85.6)[d]
	(246)	(300)	(306)			(250)	(214)	(204)		(270)	(270)
CHCl$_2$—	24.1[a]	99.2	88.8	(85)[f]	(85)[f]	(109)[c]	77.7	(60)[c]	(52)[h]		
	(205)	(263)	(270)			(211)	(176)	(164)	(163)		
CCl$_3$—	18.7[a]	96	87.7[i]	85.3[i)[k]	85.4[i)[k]	(104)	72.9	54.7			
	214	(274)	283			220	185	173			
CH$_2$Br—	40.5[a)[g]	101.7	89.7	86.7	86.9	(111)[c]	(79)[c]	(64)[c]		(97.0)[d]	(86.9)[d]
	(255)	(300)	(307)			(248)	(212)	(203)		(270)	(268)
CHBr$_2$—	54.3[a]	(103)[c]	(93.3)[c]			(113)[c]	(78)[c]	(62)[c]			
	(230)	(263)	(269)			(209)	(171)	(161)			
CBr$_3$—	(72)[a]	96[l]	(98)[c]			(115)[c]	(79)[c]	56.2[l]			
	(253)	(260)				(217)	(177)	(160)			
CH$_2$I—	54.0[a)[g]	102.7	90	86.8					51.3 [b]	(96.4)[d]	(87)[d]
	(258)	(289)	(294)						(185)	(259)	(258)
CHI$_2$—	79.9[a]	102.7[a]							45.7[a]		

[a] Ref. [68];   [b] See footnote f Table 2;   [c] Heats of formation based on the estimated data given in Ref. [71]. For reasons of consistency with more recent experimental data the estimates for mixed halomethanes containing fluorine atoms have been raised by 2 kcal mol^{-1};   [d] See footnote s to Table 4;   [e] Footnote e to Table 2;   [f] Based on estimated ΔH_f^o group values of $C(F_3)(C) \approx -168$ and $C(Cl_2)(H)(C) \approx -20$ (Ref. [29]);   [g] Ref. [69];   [h] Estimated value for $\Delta H_f^o(RX)$ based on related groups;   [i] Ref. [70];   [k] Based on a group value for $\Delta H_f^o(CCl_3C)$ of ~ -24.90[k];   [l] Ref. [72];   [m] Ref. [73].

Assuming that β-effects of saturated substituents are negligible, bonds 1,2 and 5 can be assigned the values for CH_3OCH_2–H (93.3), CH_3O–CH_3 (81.4) and n-propyl-H (98) respectively. This leaves the two bonds 4 and 6, which both involve an α-methyl substituent effect, compared with the CH_3OCH_2–X bond listed in Table 4.

The difference between n-C_3H_7–CH_3 and i-C_3H_7–CH_3 is 1 kcal mol^{-1} and consequently bond 4 is calculated to be $DH°(H_3COOCH_2$–$CH_3) - 1$ kcal mol^{-1} = 82.9 – 1 = 81.9. Bond 6 is best estimated from the corresponding t-butyl-H-bond of 92 kcal mol^{-1} reduced by an apparent α-alkoxy effect of 1 kcal mol^{-1} to give 91 kcal mol^{-1}.

c) *Hexachloroethane:* It is also possible of course to calculate BDE's which are not listed in the tables on the basis of the heats of formation of the fragments which are given in the tables, and the heat of formation of the corresponding molecules.

$$\Delta H^°_{f,298}(C_2Cl_6) = -34.5^{29)} \qquad \Delta H^°_{f,298}(\dot{C}Cl_3) = 18.7$$

This leads to $DH^°_{298}(CCl_3$–$CCl_3) = 71.9$, assuming zero activation energy for recombining CCl_3 radicals.

E. Additional selected R—H homopolar bond dissociation energies. – Selected individual homopolar bond dissociation energies, for which reliable data are available but which have not been incorporated in Tables 2–5 are summarized below.

Bond R—H	Dissociation Energy $DH^°_{298}$(R—H) kcal mol^{-1}	Ref.
$(CH_3)_3C$—H	99	[5]
cyclo-C_3CH_2—H	97.4	[77]
$\underset{O}{\boxed{}}$—H	91.5	[78]
$CH_3CH(OH)$—H	~94	a)
$CH_3CH_2\underset{\overset{\parallel}{O}}{C}$—H	87	[81]
$C_6H_5CO\underset{\overset{\parallel}{O}}{CH_2}$—H	100.2	[74]
$HCO\underset{\overset{\parallel}{O}}{CH_2}$—H	>100	[66]
F_3CCF_2—H	103	[5]
Cl_3CCCl_2—H	96	[82]
HCl_2CCCl_2—H	96	[83]
CH_3CH_2O—H	103.9	[84]
$(CH_3)_2CHO$—H	104.9	[84]
$(CH_3)_3CO$—H	105.2	[5]
CH_3OO—H	(112)	[5]
C_2H_5OO—H	(110)	[5]
HOO—H	(90)	[5]

a) Deduced from data of *Buckley & Whittle* [79] for $CH_2(OH)$—H (92) and of *Tarr & Whittle* [80] for $CH_3CH(OH)$—H (90) corrected for new value for $CH_2(OH)$—H, listed in Table 4.

F. π-bond dissociation energies. – The multiple bond strength DH°_{298} (RX_π) in olefinic $(DH^\circ_{298}(CC_\pi))$ carbonyl $(DH^\circ_{298}(CO_\pi))$ or related compounds can operationally be defined as the heat of forming the corresponding α,β-biradical as shown in equation 6.

$$\underset{R^2}{\overset{R^1}{>}}C=C\underset{R^4}{\overset{R^3}{<}} \quad\underset{-6}{\overset{6}{\longleftrightarrow}}\quad \underset{R^2}{\overset{R^1}{>}}\dot{C}-\dot{C}\underset{R^4}{\overset{R^3}{<}} \tag{6}$$
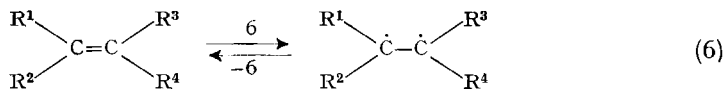
For 298 K:

$$DH^\circ_{298}(CC_\pi) = \Delta H_{298}(6) = \Delta H^\circ_{f,298}(\text{Biradical}) - \Delta H^\circ_{f,298}(\text{Molecule}) .$$

The heat of formation of the biradicals are not directly accessible from experimental data but can be estimated on the basis of the corresponding saturated hydrocarbons and the relationships given below:

$$\underset{R^2}{\overset{R^1}{>}}H{-}C_b{-}C_a{-}H\underset{R^4}{\overset{R^3}{<}} \quad\underset{-7}{\overset{7}{\longleftrightarrow}}\quad \underset{R^3}{\overset{R^1}{>}}H{-}C_b{-}\dot{C}_a\underset{R^4}{\overset{R^2}{<}} \quad +H \tag{7}$$

$$\underset{R^2}{\overset{R^1}{>}}H{-}C_b{-}\dot{C}_a\underset{R^4}{\overset{R^3}{<}} \quad\underset{-8}{\overset{8}{\longleftrightarrow}}\quad \underset{R^2}{\overset{R^1}{>}}\dot{C}_b{-}\dot{C}_a\underset{R^4}{\overset{R^3}{<}} \quad +H \tag{8}$$
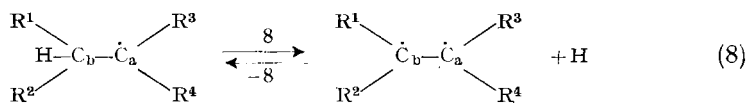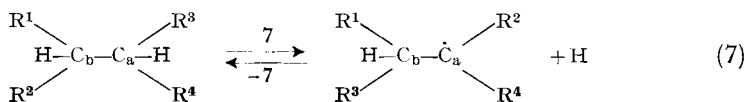
$$\Delta H^\circ_{f,T}(\text{Biradical}) = \Delta H^\circ_T(7) + \Delta H^\circ_T(8) - 2\,\Delta H^\circ_f(H) + \Delta H^\circ_f(\text{alkane}) \tag{9}$$

Assuming the activation energies for recombination of hydrogen atoms and for E_{-7} and E_{-8} to be zero results in

$$\Delta H^\circ_{f,T}(\text{Biradical}) = DH^\circ_T(C_a{-}H) + DH^\circ_T(C_b{-}H) - DH^\circ_T(H{-}H) \tag{10}$$

and

$$DH^\circ_T(CC_\pi) = DH^\circ_T(C_a{-}H) + DH^\circ_T(C_b{-}H) - DH^\circ_T(H{-}H) - \Delta H^\circ_{f,T}(\text{olefin}) + \\ + \Delta H^\circ_{f,T}(\text{alkane}) \tag{11}$$

Operationally the π-bond strength is then also defined on the basis of equations 6 to 10 as the difference in BDE's in the molecule and the corresponding mono-radical:

$$DH^\circ_{298}(CC_\pi) = DH^\circ_{298}(CC{-}X) - DH^\circ_{298}(\dot{C}C{-}X) \tag{I}$$

Equation I can then be used to derive bond dissociation energies for C–X bonds in radicals.

Equation 11 can also be written in terms of heats of hydrogenations (ΔH°_h) as:

$$DH^\circ_{298}(CC_\pi) = DH^\circ_{298}(C_a{-}H) + DH^\circ_{298}(C_b{-}H) - DH^\circ_{298}(H{-}H) + \Delta H^\circ_{h,298} \tag{12}$$

For carbonyl compounds correspondingly

$$\underset{R^2}{\overset{R^1}{>}}C=O \quad\underset{-9}{\overset{9}{\longleftrightarrow}}\quad \underset{R^2}{\overset{R^1}{>}}\dot{C}-\dot{C} \tag{13}$$

and
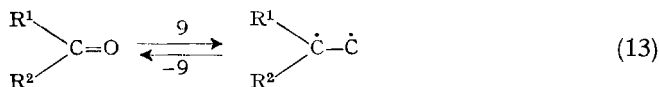
$$DH^\circ_{298}(CO_\pi) = DH^\circ_{298}(C{-}H) + DH^\circ_{698}(O{-}H) - DH^\circ_{298}(H{-}H) + \Delta H^\circ_T(9) .$$

To a first approximation the dissociation energies of the C_b–H bonds in the mono-radical and the corresponding molecule can be assumed to be equal[3]). Using for the BDE in the molecules values listed in Table 3 and 4 and calculating heats of hydrogenation ($\Delta H_{H,T}^{o}$) from the corresponding data for the heats of formation yields the π-bond dissociation energies shown in *Table 6*.

Table 6. *π-Bond energies in kcal mol^{-1} in olefinic and carbonyl compounds at 25° and 1 atm. pressure*

Compound	$DH_{298}^{o}(CC_{\pi})$	Compound	$DH_{298}^{o}(CO_{\pi})$	
C_2H_4	59.3	Cyclohexene	58.4	
C_3H_6	59.1	*cis*-Stilbene	33.1	
i-C_4H_8	57.9	Acetylene	~70	
1-C_4H_8	58.8	C≡O	68.5	[85] [4]
2-cis-C_4H_8	57.5	$H_2C=O$	72.8 a)	
2-trans-C_4H_8	58.6	$H(CH_3)C=O$	75.8 b)	
2,3-Dimethylbut-2-ene	54.1	$(CH_3)_2C=O$	77.8 c)	
1,3-Butadiene	50.4		76.6 d)	
		C=C—O—CH$_3$	59±1.5	[86]

a) Reference [64] corrected for newer data [29] of -25.95 for $\Delta H_f^{o}(CH_2O)$.

b) Based on an estimated value of 92.5 for $DH°(CH_3CHOH—H)$ yielding $\Delta H_f^{o}(CH_3CHOH \approx -15.8)$ and $CH_3\dot{C}HO—H \approx 104$ [84] yielding $\Delta H_f^{o}(CH_3\dot{C}H—\dot{O}) \approx 36.1$ kcal mol^{-1}.

c) Based on a value of -12.3 for $\Delta H_f^{o}(CH_3)_2CH—O$ [84].

d) Calculated from $\Delta H_r \approx 27.4$ for $(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2C=O + H$ [65] and from $DH°(CH_3)_2CHO—H \approx 104$ [84].

The observed substituent effects can readily be rationalized on the basis of the α,β-biradical model.

Alkyl substituents or substituents that generate 'extra' stabilization energies in one or both of the radical centers of the α,β-biradical have essentially the same effect as was observed for σ-bonds and mono radicals. For alkyl substituents it appears that both an energetic and a 'steric' effect are operative. Energetically a polarizability stabilization of about 0.8 kcal mol^{-1} per alkyl group is indicated, affecting only one, *i.e.* the positively induced olefinic carbon center. Substitution on the negatively induced carbon center has little effect, as is seen from the fact that $DH_{298}^{o}(CC_{\pi})$ for but-1-ene and *trans*-but-2-ene are about the same.

Apart from the energetic effect a 'steric' effect, *i.e.* a strain energy of ≈ 1.1 kcal mol^{-1} per *cis*-interaction is suggested by the observed difference between *cis* and *trans* but-2-ene. For 2,3-dimethylbut-2-ene a value of $59.3-20.8-2(1.1) \approx 55.3$ would be predicted, compared to 54.1 based on experimental data. The reduction of $DH_{298}^{o}(CC_{\pi})$ by *vinyl* or *phenyl* groups bonded to the olefinic centers is best evaluated on the

[3]) There are no experimental data available to back up the validity of this assumption, which has repeatedly been questioned.

basis of equation 6 by taking π-conjugation (E_π) in the molecule and 'extra' stabilization energies (E_s) in the biradical into account.

For 1,3-butadiene and stilbene this analysis yields:

$$DH^o_{298}(CC_\pi)_{1,3\text{-butadiene}} = DH^o_{298}(CC_\pi)_{1\text{-butene}} - E_{s(C=C-\dot{C}-C)} + E_\pi$$
$$= 58.8 - 12.5 + 3.5\ [87] = 49.8$$
$$\text{observed} \qquad\qquad 50.4$$

$$DH^o_{298}(CC_\pi)_{cis\text{-stilbene}} = DH^o_{298}(CC_\pi)_{cis\text{-but-2-ene}} - 2\ E_{s(C_6H_5\dot{C}H_2CH_3)} + E_\pi$$
$$= 57.5 - 2(12.5) + 2.3 = 34.8$$
$$\text{observed} \qquad\qquad 33.1$$

The data on stabilization energies (E_s) are discussed in detail in the following paper.

This implies, that the steric effect in 1,2-diphenylethane is about 1.7 kcal mol^{-1} larger when compared with cis-but-2-ene which is very reasonable. It then appears, that the very simple concept of an α,β-biradical formed by breaking a π-bond works surprising well on a quantitative basis.

In contrast to the effect on olefinic π-bonds, alkyl substituents bonded to carbonyl groups appear to increase the π-bond strength in an almost incremental manner by about 2.5 kcal mol^{-1} per alkyl group. This is not unexpected in view of 'resonance' effects originating from structures of the sort $H_3C\cdot\dot{C}=O$, i.e. from a partial electron donation by the alkyl group. The particularly pronounced 'resonance' stability of $R\text{-}\dot{C}=O$ structures becomes apparent from the fact, that the $DH^o(R\overset{\underset{\|}{O}}{C}-X)$ are practically the same whether R is $H, H_2C=CH$, phenyl or alkyl. It is then not possible to generate an allylic or benzylic resonance (of $\sim$12.5 kcal) involving the carbonyl carbon, because the 'extra' stabilization of the radical structure $C=C\text{-}\dot{C}=O$ exceeds that for $\overline{C\dot{-}C\dot{-}C}=O$.

Furthermore it is interesting to note, that the dative π-bond strength of the isoelectronic carbonyl group is about 20 kcal larger than that observed in olefinic bonds.

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