

A Method of Calculating the Heats of Combustion of Organic Compounds

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A simple method of calculating the heats of combustion of organic compounds is most useful to the practical chemist. In a previous paper (1) six specific equations have been given for calculating the heat of combustion of as many types of organic compounds. These equations are all based on the number of oxygen atoms, s , necessary to burn the compound to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. All oxygen in the compounds is used except the oxygen in the NO_2 group of nitrocompounds. The equations given previously are,

- | | | |
|-----|--------------------------------|---------------------|
| (1) | $-\text{Hc} = 52.48 s + 6,$ | for alkanes |
| (2) | $-\text{Hc} = 52.48 s + 20,$ | for alkenes |
| (3) | $-\text{Hc} = 52.48 s + 43.3,$ | for alkynes |
| (4) | $-\text{Hc} = 51.8 s,$ | for amides |
| (5) | $-\text{Hc} = 52.4 s,$ | for aromatics |
| (6) | $-\text{Hc} = 50.3 s,$ | for nitrocompounds. |

All of the equations given in this paper are based upon the reactant in its normal state at 25°C and 1 atm. and the answers are in kcal/mole.

The accuracy of these equations and the simplicity of the method warrants their extension to other types of compounds. Data recorded by Kharasch (2) for organic fluorine compounds fit the equation.

$$(7) \quad -\text{Hc} = 53.85 s,$$

if the organic fluorine compounds are burned to $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{HF}(\text{g})$. Equation (7) does not apply to compounds containing carbon and fluorine only (3, 4). Data on chlorohydrocarbons by Smith (5) and Waddington (6) are best given by

$$(8a) \quad -\text{Hc} = 53 (s-0.5),$$

for compounds without oxygen and by,

$$(8b) \quad -\text{Hc} = 52.2 s,$$

for the CHCl type compounds. The chlorine is converted to $\text{Cl}_2(\text{g})$.

The bromine compounds listed in Kablukov's (7) and Kharasch's papers fit the equation,

$$(9) \quad -\text{Hc} = 50.6 s,$$

if $\text{Br}_2(\text{l})$ is the final form of the bromine. Likewise for the iodine compounds given by Kharasch (2) the equation,

$$(10) \quad -\text{Hc} = 54 s,$$

holds if $\text{I}_2(\text{s})$ is produced.

Again using the data collected by Kharasch (2) and by Parks (8) and co-authors we find the following equations for aliphatic alcohols, aldehydes, acids, amino acids and ethers respectively.

- | | | |
|------|-----------------------|---|
| (11) | $-H_c = 51.64 s + 18$ | (alcohols) |
| (12) | $-H_c = 53.3 s + (?)$ | (insufficient data on
the aldehydes) |
| (13) | $-H_c = 51.85 s$ | (aliphatic acids) |
| (14) | $-H_c = 52.5 s$ | (amino acids) |
| (15) | $-H_c = 52.5 s + 30$ | (aliphatic ethers) |

It is readily seen that the heat of combustion of hundreds of organic compounds are given by the equation,

$$-H_c = Ms + b, \quad (\text{kcal/mole})$$

where M is 52.5 ± 2 and b varies from 0 for aromatic compounds and amino acids to 43 for alkynes. The constant M could be given with less variance except for the lowest molecular weight members of a series. The large values of b in the alkene and alkyne equations are undoubtedly due to the unsaturated compounds being unstable. However, with these exceptions the equation,

$$-H_c = 52.5 s$$

will give heats of combustion data accurate enough for all types of chemical work where factors such as heat transfer, radiation losses, etc., are involved. It is accurate enough to distinguish between ΔE and ΔH . This equation is not simply three times the heat of combustion of $-CH_2-$, with the heat of formation of $-CH_2-$ neglected. Our calculated value is within 1% of the correct answer for $CH_3COOH(1)$, yet the heat of formation of acetic acid is over 50% of the value of its heat of combustion.

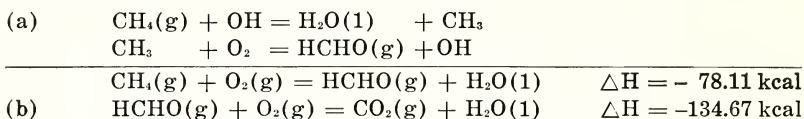
The fact that one simple equation will give results within a few per cent of accurate experimental data, regardless of the number of CO_2 molecules produced per one mole of H_2O , and regardless of the number of kind of bonds broken, or the position of a group in the molecule, indicates that the theoretical work on bond energies based upon thermochemical data needs further investigation.

The mechanism given by Lewis and von Elbe (10) for the combustion of methane led us to break up the oxidations of the various types of compounds into steps. Since the heat liberated in many of these processes is so near 105 kcal per mole of oxygen used, these stepwise processes may be the physical significance of the constant 52.5. The only radical exception to this hypothesis involves data on $HCHO(g)$ and therefore its heat of combustion is being experimentally determined in our laboratory. In order to show this relationship let us consider the following classes of compounds. All calculated values in this theoretical discussion use the general equation $-H_c = 52.5 s$ and not the specific equations since we are trying to show the origin of M .

Alkanes:

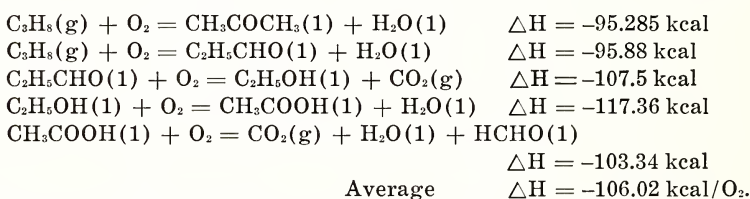
It is impossible to discuss each alkane. It is sufficient to use two, CH_4 and C_3H_8 . CH_4 is chosen because it does not fit our equation well.

The experimental value (6) is -212.80 and our calculated value is -216.0 kcal/mole. (All data from reference 11)



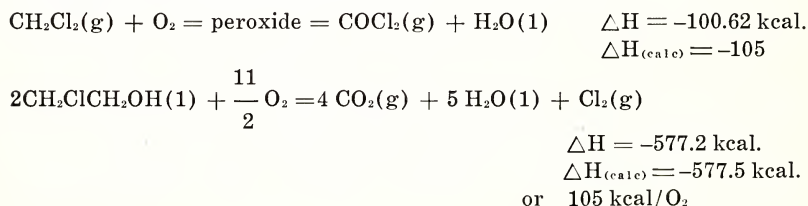
The summation of equations (a) and (b) gives the complete combustion of CH_4 and -212.78 kcal, or an average of 53.2 kcal/atom of oxygen converted to H_2O and/or CO_2 .

If the H_t of formaldehyde agreed with the one calculated using our H_c , equation (a) would be -107.8 and (b) -105.0 kcal. It does not agree with calculated results using bond energies either. Most values for the $\text{C}=\text{O}^{12,13}$ bond are taken from the heat of combustion of formaldehyde.

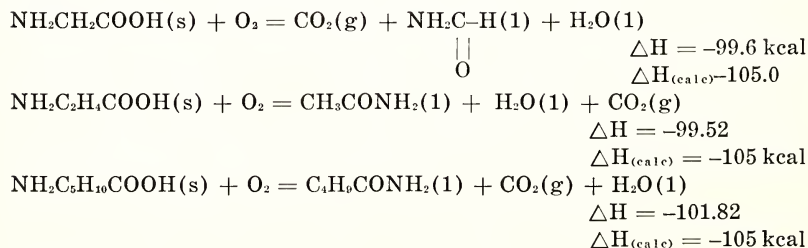


Each of these five steps assumes an intermediate peroxide. The experimental H_c of C_3H_8 is -530.6 and equation 1 gives -530.8 kcal. Note that aldehydes, ketones, alcohols and acids are included in these processes even though they usually fit the general equation very poorly.

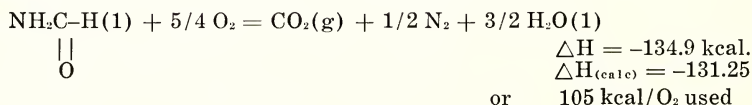
Halohydrocarbon:

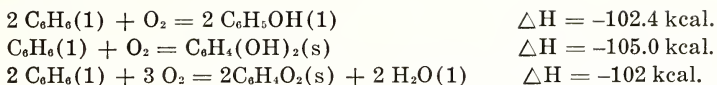


Amino Acids:



Amides:



Benzene Series:

The next step in the process is apparently a complete breakdown of the ring to give CO_2 and H_2O . The experimental ΔH for the combustion of benzene is -787.2 kcal and our calculated value is -786.0 .

Alkenes and Alkynes:

Lewis and von Elbe (10) make the statement, "the oxidation of acetylene appears to be unrelated to the reaction in other hydrocarbon-oxygen systems." They give mechanisms for ethylene involving HCHO and $\text{H}_2\text{C}-\text{CH}_2$. These mechanisms do not substantiate our theory. Mech-



anisms for ethylenes which involve $(\text{HCOH})_2$, $(\text{HCO})_2$ and $(\text{COOH})_2$, etc., necessitate a value of b equal to 20 in equation (2). If the heat of formation of alkenes and alkynes were negative instead of positive, i.e. if they were in a lower energy state, this discrepancy would not occur. Apparently we are not starting with them in a ground state comparable to the other hydrocarbons. The same difficulty occurs with the lowest molecular weight members of any series.

Bond energies (12) are discussed so much by organic chemists and chemists working on molecular structure that we are including here examples of heats of combustions calculated using bond energy data (13) and a new set of bond energies based upon thermochemical data given by Rossini (11).

In discussing the equation $-\text{Hc} = 52.5$ s, Glasstone¹² says, "A more fundamental approach to the problem of calculating heats of formation and reaction is by the use of bond energies." The futility of bond energies is exemplified by the fact that the heats of combustion of aliphatic acids are almost identical to the heats of combustion of alkanes with one less carbon. The same is true for amino acids and the corresponding amines; i.e., splitting out CO_2 absorbs about 1 or 2 kcal. The heat of combustion of glycols is almost the same as the heat of combustion of the product which remains after water is split out. Examples are:

(Kharasch's² Data)

	ΔH		ΔH
CH_3COOH	-209 kcal.	$\text{CH}_2(\text{COOH})_2(s)$	-206.5
CH_4	-210.8	$\text{CH}_4(g)$	-210.8
$\text{C}_2\text{H}_5\text{COOH}$	-367.2	$\text{CH}_2\text{OHCH}_2\text{OH}$	-281.9
C_2H_6	-368.4	CH_3CHO	-279.0
$\text{C}_3\text{H}_7\text{COOH}$	-524.3	$\text{CH}_3\text{CHOHCH}_2\text{OH}$	-431.0
C_3H_8	-526.3	CH_3COCH_3	-430.8

Bond energies are not usable unless the correct structural formula is known. The calculations are slow and tedious. We feel that the bond

energies given in Table II are more useful than those given by Glasstone (13) since we do not have to consider resonance. Bond energies cannot be meaningful except in the case of two univalent elements, i.e., the value of a C-H bond must depend on what is sharing the other 3 valences of carbon. Table I shows that the equation, $-H_c = M_s + b$ is as accurate as any system of bond energies. There are too many types of bonds for the method of bond energies to be used generally. The nitrocompounds are a striking example. The values we list are energies liberated when the two elements unite to form the bond. We do not think it is plausible for the C—C bond to have a negative value unless other elements are joined to each carbon. How can the C=C bond be more stable than the C—C bond (see Glasstone's values)? How can the C≡C be more stable than the C=C bond? We give the values of H₂O(1) and CO₂(g) since they occur in every calculation and as the data show, joining two hydrogens to oxygen is not twice the value of joining one. Likewise our C—H bond is one-fourth the heat liberated when CH₄ is formed from C and 4 H's and will have little value in CH₂F₂, CH₂(NO₂)₂, etc.

The combustion of carbon compounds in many cases is a cyclic process, compound₁ + O₂ → intermediate → compound₂ + H₂O and/or CO₂ + 105 kcal. Then the stepwise process repeats until CO₂ and/or H₂O are the ultimate products with 105 kcal liberated for each mole of oxygen consumed. This leads to the general equation,

$$-H_c = 52.5 s, \quad (\text{kcal/mole})$$

for the heat of combustion of carbon compounds.

TABLE I

Compound	Hc(expt)	Hc(calc) ₁	Hc(calc) ₂	Hc(calc) ₃
C ₂ H ₂ (g) (acetylene)	-310.6	-305.8	-309.0	-301.8
C ₂ H ₄ (g) (ethylene)	-331.6	-335	-314	-311.6
CH ₃ COOH(1) (Acetic acid)	-209.4	-207.5	-211.35	-198.1
C(NO ₂) ₄ (1) (tetranitromethane)	-102.9	-100.6	-41.7	
C ₆ H ₆ (1) (benzene)	-787.2	-787.5	-804	-760.6
CH ₂ Cl ₂ (g) (dichloromethane)	-134.3	-132.5	-139.8	-130.6
NH ₂ CH ₂ COOH(s) (glycine)	-234.0	-236.1	-235.5	-235.1
HCONH ₂ (formamide)	-134.9	-129.5	-140.0	-121.8
C ₆ H ₁₄ (1) (hexane)	-990.0	-1003.0	-1015.5	-928.6
HCHO(g) (formaldehyde)	-134.1	-106.6	-106.1	-134.8
C ₇ H ₁₅ F(1) (N-heptyl fluoride)	-1121.5	-1130.8	-1088.6	
C ₂ H ₅ OH(1) (ethyl alcohol)	-327.6	-328.0	-327.6	-315.9
C ₂ H ₄ ClOH(1) (monochloroethanol)	-288.6	-287.1	-290.2	-274.4

₁—Equations this paper, ₂—our bond energies, and ₃—Glasstone's bond energies.

This table includes a wide variety of structures and bond types. If Hc can be calculated without cognizances of structure, bond angle, or bond length, then the authors feel that heats of combustion data cannot be used to show bond structure or bond energies?

TABLE II
Bond Energies of Formation

C—C	+ 7.5	H—Cl	—103
C=C	+ 23.6	H—Br	— 87.46
C≡C	+ 42	H—I	— 71.38
C—F	— 59.0	H—H	—104.2
C—Cl	— 35.5	O=O	—118.3
C—Br	— 71.38	O—H	—101.3
C—I	— 12.0	H ₂ O(1)	—231.7
C—H	— 56.75	CO ₂ (g)	—212.4
C—O	— 60 (alcohols, acids, esters)	N≡N	—171.2
C=O	— 94.0 (ketones)	N=O	— 90 (nitro)
C≡O	— 86.0 (CO gas)	F—F	— 36.6
C=O	—106.2 (aldehydes, acids)	Cl—Cl	— 58
N—H	— 78.7	Br—Br	— 53.4
C—N	— 37	I—I	— 51
H—F	—134.6	N—F	— 55

(Values given are kcal liberated at 25°C when the bonds are formed; i.e., $H + H = H - H$ and ΔH is —104.2 cal. meaning a stable union.)

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