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A New Generalized Bond Energy/Group Contribution Scheme for Calculating the Standard Heat of Formation of Monomers and Polymers. Part V. Oxygen Compounds*

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ABSTRACT

The new generalized bond energy scheme has been extended to organic oxygen compounds. About 50 different types of bonds have been identified and their $\Delta H_f^\circ(g)$ contributions and atomization energies evaluated by a procedure similar to multilinear regression analysis. Recent thermochemical data (1969-1973) on 145 oxygen compounds and about 80 ring compounds have been employed to test the efficiency of the scheme in predicting the gas phase heats of formation. This was found to be about ± 0.8 kcal/mole, which is quite comparable to the group contribution method of Benson and co-workers involving a much larger number of parameters.

The typical chemical bonds identified and resolved in respect of their bond energies bear good consistency and correlation with bond lengths and force constants measurable independently. Heats of formation and polymerization on about 47 monomer-polymer systems and enthalpies of other polymeric reactions have been predicted and compared with available experimental data.

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INTRODUCTION

In continuation to the earlier work on hydrocarbons and halogenated hydrocarbons [1a-d], oxygen compounds have been analyzed and correlated in this paper and the generalized bond energy scheme is developed further to predict the gas phase heats of formation of compounds containing C, H, F, Cl, Br, I, and O atoms, including polymers. The source for experimental enthalpies of formation has been mainly the work of Cox and Pilcher [2] and a recent paper from Benson and co-workers [3a] about their revised group-additivity parameters for oxygen compounds. In addition, the recent thermochemical literature has been surveyed to 1973, and this led to the revision of some of the earlier established additivity parameters. The utilization of this newer and more precise data was advantageous to the evaluation of parameters for oxygen compounds. The concept of transferability and additivity of the energy parameters has now been well established by the previous work [1-3]. In this report the bond-wise distribution of the chemical energy, rather than the group-wise contribution, has been primarily aimed at and performed so as to ascribe the heat of formation (and later, other thermodynamic properties, such as C_p° and S°) or the atomization energy to a more fundamental entity; namely, the chemical bond. Although Benson and Buss in their original review [3b] considered the bond-wise approach as less precise than the group contribution procedure, the reader may find from this work that with much smaller number of bond energy terms, an equivalent (or perhaps slightly better) precision can be attained. The bond energy scheme is, in addition, simpler to assimilate and use than the group contribution approach with the implied concept of a hypothetical disproportionation reaction.

The Cox-Pilcher monograph [2] deals with a self-consistent set of bond energy terms under the Laidler method but the terms are insufficient, for the required precision and the absolute energy values (atomization energies) of many of the terms are not quite compatible with other basic properties of the bond (such as force constant and bond length); for instance, a single value for $C=O$ in both carbonyl and carboxyl types of bonds, and a rather high value of ΔH_a for $C\equiv C$ bonds. The bond energies (E°) in the present scheme are in fairly good harmony with the bond lengths and force constants based on Sutherland's relation [4a] as extended by Fox and Martin [4b] and further modified by Somayajulu [5]. Equations for the ring strain in small rings, (3-, 4-, and 5-membered), earlier developed for hydrocarbons [1c], have been revised to accommodate the introduction of oxygen atom in the ring structure. The new scheme is tested only with the recent experimental data

accrued following publication of the Cox-Pilcher monograph (1968), and the overall precision attained was found to be ± 0.8 kcal/mole and generally within 1 kcal/mole, even for monocyclic rings.

DERIVATION OF ENERGY TERMS

Basic Bond Contribution

Table 2 lists the energy terms for various bonds identified in oxygen compounds. The first 11 terms relate to the simple carbon-oxygen covalent single bond of ethers, alcohols, and phenols, for which relatively very accurate thermochemical data are available. The strength of the C—O bond depends both on the hybridization of the C atom (denoted by superscripts: C^3 , C^2 , C^ϕ , etc.) as well as on the number of hydrogen atoms present on it (denoted by subscripts: C_1 , C_2 , etc.). The notation employed in regard to subscripts in the previous parts of this work, which was based on the subscripts indicating the number of C atoms to which the subject carbon atom was bonded, has now been changed. The number of hydrogens present on the carbon atom has more relevance in oxygen and nitrogen compounds because of hydrogen bonding and other polar and inductive interactions. Thus such former symbols as C_1^3 , C_2^3 , and C_3^3 , denoting the groups $-\text{CH}_3$, $-\text{CH}_2$, and $-\text{CH}$, respectively, are now presented as C_3^3 , C_2^3 , and C_1^3 in this and future parts of the scheme. The term $C^3-\text{O}''$ (Nos. 9 to 11 in Table 2) pertains to the carbon atom linked to two oxygens by ethereal linkages and has been derived from polyoxymethylene and a few other essentially strain-free 6-membered, 1,3-dioxanes and similar rings. In the present scheme it has been implicitly assumed that these ethereal bonds exist in all related compounds such as alcohols and esters, and that they possess the same energies as in ethers. This special feature of the scheme is justified by the consistency of the end results. It has resulted in much economy in the number of new energy parameters invoked. Thus all alcohols (primary, secondary, tertiary), phenols, and acids could be well correlated by a combination of the appropriate value of the ether linkage and the common value of -26.4 kcal/mole for the O—H bond. All esters from these alcohols were also fitted in satisfactorily.

The energy term for the carbonyl $C^2=\text{O}$ bond in ketones was estimated at -22.3 ± 0.5 kcal/mole, employing all other energy terms from the earlier work [1]. Using the same energy term for the aldehyde $C^2=\text{O}$, two further terms were found necessary, one for the $(\text{O})C^2-\text{H}''$ in formaldehyde and the other for $(\text{O})C^2-\text{H}'$ in all other aldehydes. The energy values for these bonds indicate

that the C^2-H in aldehydes is considerably weaker than in the corresponding hydrocarbons. The group contribution for the $-COOH$ group in carboxylic acids was found to be -88.5 ± 1.0 kcal/mole, the larger standard deviation being mainly due to the uncertainty in the enthalpies of sublimation of these polar and H-bonded compounds, as well as to the paucity of such data. Similarly, the group contributions for the anhydride ($OC-O-CO$) and the carbonate (OC^{\ominus}) groups were -109.0 ± 2 and -94.0 ± 1.5 kcal/mole, respectively; the higher uncertainty limits arising from the paucity of data on phase-change enthalpies, and thus empirical estimates of these quantities by the methods of Small [6a] and Bondi [6b] had to be employed. Some of the newer experimental data in Table 3 was of much help in deciding upon a firm value for the carbonate group where some of the experimental work [63] appears to be in error.

Since the present scheme is based on the concept of the transferability of individual bond energy rather than the group contribution, it was necessary to see whether the above three group values for $-COOH$, $OC-O-CO$ and OC^{\ominus} moieties could be split up into a self-consistent set of individual bond energy terms applicable to all acids, anhydrides, esters, acid halides, etc. The carboxyl $C^2=O$ in acids and acid derivatives is conceptually higher than the carbonyl $C^2=O$ of aldehydes and ketones, as evidenced by the correlation with force constants and bond lengths given in Table 1. The magnitude of the carboxyl $C^2=O$ was fixed at -33.3 kcal/mole, a value about 11 kcal higher than the ketonic $C^2=O$, in harmony with the modified Sutherland relationship [4, 5]. The value for the carbonate $C^2=O$ was similarly found to be -36.4 ± 1.0 kcal/mole, envisaging a still stronger bond because of its resonant association with two oxygen atoms (a higher oxidation state) as against one in the carboxyl $C^2=O$. The same bond is pertinent to ketene and carbon suboxide due to the higher delocalization of the double bond. Much economy of parameters and consistency has resulted from assigning different values for the $C^2=O$ bond, although it may be entirely possible to have one single value for the $C^2=O$ but many more energy terms for other bonds as in the Laidler scheme as expanded by Cox and Pilcher [2]. We thus have three different values for $C^2=O$ as terms Nos. 15, 16, 17, and 18 in Table 2. The bond strengths of $C^2=O$ in carbon dioxide and carbon monoxide are still higher but maintain a good consistency with the Sutherland relationship. The $(O)C^2-O$, the "short bond" in acids and esters, was estimated at -28.8 ± 0.5 kcal/mole, which is also consistent with Sutherland relationship.

The $[(\text{O})\text{C}^2-\text{O}]''-\text{O}$ bond in anhydrides was found to be -21.2 ± 2 kcal/mole, a value considerably lower but explaining the ease of hydrolysis. The short bond of the acids and esters precisely applies to the carbonate ester also, when combined with the appropriate recommended value of -36.4 kcal/mole for $\text{C}^2=\text{O}$. The $\text{C}^2=\text{O}$ bond in acid halides is necessarily the carboxyl, rather than the carbonyl, since the latter would require very high values for the carbon-halogen bonds, which would be quite inconsistent with the ease of hydrolysis of the acid halides. In carboxyl dihalides, e.g., phosgene- COCl_2 , the carboxyl carbon is associated with two strongly electronegative atoms as in the carbonate $\text{O}=\text{C}^0$, which dictates a value of -36.4 kcal/mole for the carboxyl double bond in phosgene and other dihalides, combined with normal values of carbon-halogen bonds (viz., terms Nos. 34, 36, 38, and 39 in Table 2). Alternately, if a lower value of -33.3 kcal/mole is preferred for the carboxyl double bond, such special terms as Nos. 33, 35, and 37 in Table 2 for the $(\text{O})\text{C}^2-\text{X}''$, similar to $(\text{O})\text{C}^2-\text{H}''$ of formaldehyde, must be invoked. Both these independent routes lead to almost the same value of $\Delta H_f^\circ(\text{g})$ for a carboxyl dihalide.

The strength of a C^2-C^2 in butadiene or a C^1-C^2 in propyne (cf. Part II [1b]) originates from resonance or delocalization of π -electrons over the entire molecule. The energy terms of such hydrocarbons are, however, not applicable, vis-à-vis, to the sp^2 -carbon in carbonyl or carboxyl group in oxygen compounds. The energy terms of $\text{C}^1-\text{C}^2(\text{O})$ and $\text{C}^2-\text{C}^2(\text{O})$ bonds are somewhat lower in energy as seen from terms Nos. 24, 25, 26, and 27 in Table 2. The bond strength of $(\text{O})\text{C}^2-\text{C}^2(\text{O})$, the link between two carbonyls as in diacetyl, is substantially lower, and the bond between two carboxyls, $(\text{OO})\text{C}^2-\text{C}^2(\text{OO})$, in oxalic acid even assumes a positive value for $\Delta H_f^\circ(\text{g})$, explaining the easy oxidation and dissociation of oxalic acid. Molecular models of oxalic acid or its derivatives do not show any steric factor, but the C^2-C^2 bond seems to be intrinsically weaker in energy. The esters of phenol (and other aryl alcohols) required a special energy term (No. 12) for $\text{C}^\phi-\text{O}(\text{CO})$, the ester long bond, although the usual values of the $\text{C}-\text{O}$ linkage as derived from corresponding ethers worked well for all other esters. Malonic acid has a methylene bridge between the two carboxyls, similar to a carbon atom (C^2 , C^1 , or C^0) bridging two oxygens in some di-ethers and special energy term No. 23 of Table 2, for $\text{C}^3-[\text{C}^2(\text{OO})]''$ bond was necessary, analogous to terms Nos. 9, 10, and 11 for ethers.

TABLE 1. Fundamental Properties of Some Typical Chemical Bonds Identified in the Bond-Energy Scheme and Their Correlation

No.	Bond	Bond energy (E°), (kcal/mole)	Bond length (r), (\AA)	Force constant (k), (md/ \AA)	Sutherland's constant $\left(S_{ij} = \frac{kr^2}{E^{\circ}}\right)$, arbitrary units	Vibration frequency (ν_{str}), (cm^{-1})	Key compound
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	$\text{C}^{\text{s}}-\text{C}^{\text{s}}$	85.2	1.543	4.45	12.4	900	Ethane
2	$\text{C}^{\text{t}}-\text{C}^{\text{s}}$	90.0	1.501	4.42	11.1	920	Propylene
3	$(\text{O})\text{C}^{\text{t}}-\text{C}^{\text{s}}$	90.0	1.504	4.63	11.6	1105	Acetaldehyde
4	$(\text{OO})\text{C}^{\text{t}}-\text{C}^{\text{s}}$	90.0	1.497	4.50	11.2	996	Acetic acid
5	$\text{C}^{\text{t}}-\text{C}^{\text{t}}$	89.8	1.508	4.69	11.9	1009	Toluene
6	$\text{C}^{\text{t}}-\text{C}^{\text{t}}$	98.6	1.465	4.8	10.4	1205	Butadiene
7	$(\text{O})\text{C}^{\text{t}}-\text{C}^{\text{t}}$	97.2	1.470	5.0	11.1	(1060) ^a	Acrolein
8	$(\text{OO})\text{C}^{\text{t}}-\text{C}^{\text{t}}$	97.2	1.44	(5.2) ^a	11.1	1240	Acrylic acid
9	$(\text{O})\text{C}^{\text{t}}-\text{C}^{\text{t}}(\text{OO})$	89.2	1.47	(4.5) ^a	10.9	1060	Glyoxal
10	$(\text{OO})\text{C}^{\text{t}}-\text{C}^{\text{t}}(\text{OO})$	81.1	1.54	(4.4) ^a	(12.9)	995	Oxalic acid
11	$\text{C}^{\text{t}}-\text{C}^{\text{t}}$	96.4	1.48	4.8	10.9	1203	Styrene

(A) Carbon-Carbon Bonds

12	$(O)C^2-C^\phi$	95.6	1.48	4.50	10.3	1206	Benzaldehyde
13	$(OO)C^2-C^\phi$	95.6	1.48	(5.2) ^a	11.8	1070	Benzoic acid
14	$C^\phi-C^\phi$	96.4	1.498	4.58	10.6	1275	Biphenyl
15	C^1-C^3	100.6	1.462	5.30	11.3	1382	Propyne
16	C^1-C^2	107.3	1.448	(6.0) ^a	11.7	1168	Vinyl acetylene
17	$C^1-C^2(O)$	93.6	1.445	4.1(?)	(9.4)	944	Propynal
18	$C^1-C^2(OO)$	93.6	1.43	-	-	-	Acetylene dicarboxylic acid
19	C^1-C^ϕ	105.8	1.432	5.5	10.7	1192	Ethynyl benzene
20	C^1-C^1	118.6	1.379	7.14	11.5	1235	Diacetylene
21	$C^\phi-C^\phi$	118.4	1.379	7.6	12.5	1585	Benzene
22	$C^\phi-C^\phi$	114.3	1.425	(7.0) ^b	(12.5)	(1520) ^a	Naphthalene
23	$C^\phi-C^\phi$	112.7	1.436	(6.8) ^b	(12.5)	(1500) ^a	Anthracene
24	$C^2=C^2$	133.3	1.339	9.57	12.9	1630	Ethylene
25	$(C)C^2=C^2$	133.3	1.336	9.01	12.1	1620	Propylene
26	$C_0^2=C^2$	135.3	1.309	10.8	13.7	1980	Allene
27	$C_0^2=C_0^2$	147.5	1.284	(10.6) ^a	11.8	2079	Butatriene
28	$C^1\equiv C^1$	170.9	1.20	15.8	13.3	2120	Acetylene

(continued)

TABLE 1 (continued)

No.	Bond	Bond energy (E°), (kcal/mole)	Bond length (r), (Å)	Force constant (k), (md/Å)	Sutherland's constant $(S_{ij} = \frac{kr^2}{E^{\circ}})$, arbitrary units	Vibration frequency (ν_{str}), (cm^{-1})	Key compound
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
29	(C)C ¹ ≡C ¹	170.9	1.204	15.87	13.5	2142	Propyne
30	(C ²)C ¹ ≡C ¹	170.9	1.209	15.40	13.2	(2100) ^a	Propynal
						Mean: 11.8 ± 1.0	
<u>(B) Carbon-Hydrogen Bonds</u>							
1	C ³ -H ¹¹¹	98.4	1.102	4.90	5.96	2960	Ethane
2	C ² -H ¹¹	101.3	1.085	5.20	6.04	3060	Ethylene
3	C ₆ ² -H ¹¹	101.3	1.069	5.16	5.82	3061	Allene
4	(O)C ² -H ¹¹	96.7	1.111	4.33	5.52	2851	Formaldehyde
5	(O)C ² -H	97.4	1.114	4.88	6.22	2822	Acetaldehyde
6	(OO)C ² -H	97.4	1.106	4.69	5.89	2943	Formic acid
7	C ^φ -H	101.7	1.084	5.2	6.01	3062	Benzene
8	(C)C ² -H ¹	100.6	1.090	5.02	5.93	3081	Propylene

9	C ¹ -H	110.8	1.06	5.91	5.98	3217	Acetylene
10	(C)C ¹ -H	110.8	1.055	5.94	5.97	3326	Propynal
					Mean: 5.9 ± 0.2		
<u>(C) Carbon-Halogen Bonds</u>							
<u>Carbon-Fluorine</u>							
1	C ³ -F	105.6	1.333	5.96	10.0	1100	Ethyl fluoride
2	C ² -F	110.4	1.33	6.4	10.3	1080	Vinyl fluoride
3	(O)C ² -F"	118.1	1.328	6.85	10.2	965	Carbonyl fluoride
4	C ^φ -F'	112.5	1.327	7.9	12.4	806	Fluorobenzene
5	C ¹ -F	(115)	1.275	8.60	12.2	1055	Fluoroacetylene
					Mean: 11.0 ± 1.0		
<u>Carbon-Chlorine</u>							
6	C ³ -Cl	84.5	1.767	3.64	13.5	650	Ethyl chloride
7	C ² -Cl	84.7	1.726	3.8	13.4	720	Vinyl chloride
8	(O)C ² -Cl"	81.4	1.746	3.7	13.9	568	Carbonyl chloride
9	C ^φ -Cl'	86.2	1.70	3.56	11.9	710	Chlorobenzene
10	C ¹ -Cl	(100)	1.632	5.35	14.2	756	Chloroacetylene
					Mean: 13.1 ± 0.9		

(continued)

TABLE 1 (continued)

No.	Bond	Bond energy (E°), (kcal/mole)	Bond length (r), (\AA)	Force constant (k), (md/ \AA)	Sutherland's constant $\left(S_{ij} = \frac{kr^2}{E^\circ}\right)$, arbitrary units	Vibration frequency (ν_{str}), (cm^{-1})	Key compound
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
<u>Carbon-Bromine</u>							
11	C^3-Br	71.0	1.938	2.9	15.3	560	Ethyl bromide
12	C^2-Br	70.4	1.86	(3.0)	14.7	612	Vinyl bromide
13	$(\text{O})\text{C}^2-\text{Br}$	66.5	2.05	2.57	16.2	425	Carbonyl bromide
14	$\text{C}^\phi-\text{Br}'$	71.0	1.865	3.12	15.3	671	Bromobenzene
15	C^1-Br (80 μ)		1.80	4.48	18.1	618	Bromoacetylene
16	C^1-Br	(80)	1.793	4.60	18.5	(626) ^a	Bromopropynal
					Mean: 16.3 ± 1.5		
<u>Carbon-Iodine</u>							
17	C^3-I	56.3	2.135	1.91	15.5	500	Ethyl iodide
18	C^2-I	55	2.091	1.80	14.3	514	Vinyl bromide
19	$\text{C}^\phi-\text{I}$	55.4	2.08	2.52	19.7	654	Iodobenzene

20	C ¹ -I	(56)	1.99	3.75	26.5	600	Iodoacetylene
21	C ¹ -I	(56)	1.991	3.00	21.2	670	Iodopropynal
						Mean: 20 ± 5	
<u>(D) Carbon-Oxygen Bonds</u>							
1	C ³ -O	84.0	1.416	5.09	12.2	940	Dimethyl ether
2	C ³ -O	84.0	1.427	5.22	12.7	1034	Methanol
3	C ² -O	95.8	1.325	(6.0) ^a	11.2	1219	Methyl vinyl ether
4	(C ²) ⁿ -O	93.8	1.42	(5.5) ^a	11.8	1200	Divinyl ether
5	(O)C ² -O	101.4	1.33	6.0	10.5	1093	Formic acid "short bond"
6	(O)C ² -O ⁿ	101.4	1.33	(6.1) ^a	10.5	1100	Ethylene carbonate
7	C ^ϕ -O	95.8	1.379	5.7	11.0	1261	Phenol
8	C ^ϕ -O(CO)	89.6	-	-	-	-	Phenyl ester
9	(C ^ϕ) ⁿ -O	93.2	1.28	-	-	-	Diphenyl ether
10	C ² =O	167.5	1.213	12.1	10.6	1177	Formaldehyde
11	C ² =O	167.5	1.216	11.6	10.2	1113	Acetaldehyde
12	C ² =O	167.5	1.24	11.4	10.4	1067	Acetone
13	(F ⁿ)C ² =O	178.5	1.174	14.6	11.3	1928	Carbonyl fluoride

(continued)

TABLE 1 (continued)

No.	Bond	Bond energy (E°), (kcal./mole)	Bond length (r), (\AA)	Force constant (k), (md./ \AA)	Sutherland's constant $\left(S_{ij} = \frac{kr^2}{E^{\circ}}\right)$, arbitrary units	Vibration frequency (ν_{str}), (cm^{-1})	Key compound
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
14	(Cl ¹¹)C ² =O	178.5	1.166	14.2	10.6	1827	Phosgene
15	(Cl)C ² =O	178.5	1.192	13.0	10.3	1869	Acetyl chloride
16	(O)C ² =O	178.5	1.228	13.2	11.2	1770	Formic acid
17	(O)C ² =O	178.5	1.245	12.4	10.8	1748	Acetic acid
18	(OO)C ² =O	181.6	1.17	(14.2) ^a	10.7	1870	Ethylene carbonate
19	C ₆ ² =O	181.6	1.16	14.9	11.0	2150	Ketene
20	C ₆ ² =O	181.6	1.16	14.2	10.5	2230	Carbon suboxide
21	C ₆ ² =O ¹¹	187.2	1.163	15.5	11.2	2349	Carbon dioxide
22	C ¹ ...O	197.7	1.128	19.0	12.2	2146	Carbon monoxide
					Mean: 11.0 \pm 0.7		
(E) Oxygen-Hydrogen Bonds							
1	(C)O-H	108.3	0.956	7.62	6.4	3680	Methanol
2	(C ^{ϕ})O-H	108.3	0.944	(7.5)	6.2	3612	Phenol

3	(OC)O-H	108.3	0.984	7.27	6.5	3570	Formic acid
4	(O)O-H	110.8	0.98	8.11	7.0	3417	Hydrogen peroxide
5	O-H''	110.8	0.967	8.46	7.0	3694	Water

Mean: 6.6 ± 0.4

(F) Oxygen-Oxygen Bonds

1	(H)O-O(H)	34.4	1.483	4.01	25.6	880	Hydrogen peroxide
2	(OC)O-O(H)	35.0	1.49	4.28	27.0	(905) ^a	Performic acid
3	O-O''	42.6	1.217	7.44	28.2	1043	Ozone
4	O=O	59.6	1.207	11.8	28.7	1580	Oxygen

Mean: 27.4 ± 1.2

(G) Hydrogen-Halogen and Interhalogen Bonds (diatomic molecules)

1	H-F	132.6 (135.6) ^c	0.917	9.96	6.1 (6.0) ^c		Hydrofluoric acid
2	H-Cl	103.2	1.275	5.16	8.1	2886	Hydrochloric acid
3	H-Br	87.5	1.414	4.12	9.4	2558	Hydrobromic acid
4	H-I	71.3	1.604	3.14	11.4	2238	Hydriodic acid

(continued)

TABLE 1 (continued)

No.	Bond	Bond energy (E°), (kcal/mole)	Bond length (r), (\AA)	Force constant (k), (md/ \AA)	Sutherland's constant $\left(S_{ij} = \frac{kr^2}{E^{\circ}}\right)$, arbitrary units	Vibration frequency (ν^{str}), (cm^{-1})	Key compound
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
5	F-F	30.9 (37.0) ^c	1.418	4.45	29.0 (24.2) ^c	892	Fluorine
6	F-Cl	59.5 (62.5) ^c	1.628	4.56	20.3 (19.3) ^c		
7	F-Br	56.2 (59.2) ^c	1.756	4.1	22.5 (21.4) ^c		
8	F-I	63.3 (66.3) ^c	2.05	3.64	24.2 (23.1) ^c		
9	Cl-Cl	58.0	1.988	3.3	22.5	565	Chlorine
10	Cl-Br	(?)	2.138	2.72			
11	Cl-I	50.4	2.321	2.38	25.4		
12	Br-Br	53.5	2.283	2.5	24.4	323	Bromine
13	Br-I	42.5	2.434	2.06	28.7		
14	I-I	51.0	2.667	1.7	23.7	215	Iodine

Mean: 23.7 ± 2 for interhalogen bonds

(H) Summary of Sutherland's Constants (S_{ij})

No.	Bond type	Energy range (kcal/mole)	(S_{ij}), arbitrary units	Reduced atomic mass (μ), arbitrary units	($S_{ij}/\sqrt{\mu}$), arbitrary units
1	C-C	81-171	11.8 ± 1.0	6.00	4.8
2	C-H	97-111	5.9 ± 0.2	0.92	6.1
3	C-F	105-118	11.0 ± 1.0	7.35	4.1
4	C-Cl	81-100	13.1 ± 0.9	8.97	4.4
5	C-Br	66-80	16.3 ± 1.5	10.43	5.0
6	C-I	55-56	20 ± 5	10.96	6.0
7	C-O	84-198	11.0 ± 0.7	6.86	4.2
8	O-H	108-111	6.6 ± 0.4	0.94	6.8
9	O-O	34-60	27.4 ± 1.2	2.83	9.7
10	Hal-Hal	37-58	(23.7 ± 2) _{av}	(32.5) _{av}	(4.2) _{av}
11	H-Hal	71-136	6 to 12	1.0	6 to 12
12	H-H	104.2	3.0	0.50	4.2

^aValue interpolated from $(\nu_{\text{str}})^2$ vs (force constant) curve for the type of bond.

^bValue predicted from the overall average S_{ij} for the type of bond.

^cThe bond dissociation energy of fluorine is still in serious controversy in view of a recent paper by Gole and Margrave [106] who support a value of 36 to 37 kcal/mole. This value has been used for parenthesized figures for fluorine bonds. A general revision for earlier work [1d] is necessary.

TABLE 2. Bond-Energy Terms and Strain Energies for Calculating the Heat of Formation (gas, 25°C) of Oxygen Compounds

No.	Bond ^a	ΔH_f° (g) (kcal/mole)	Bond strength (E_{25}°), (kcal/mole)	Compounds from which derived: references
(1)	(2)	(3)	(4)	(5)
1	C^3-O	-11.4	84.0	Ethers and alcohols
2	C^2-O	-14.5	87.1	Ethers and alcohols
3	C^1-O	-16.8	89.4	Ethers and alcohols
4	C^0-O	-18.0	90.7	Ethers and alcohols
5	C^2-O	-23.2	95.8	Ethers and alcohols
6	$C^\phi-O$	-23.2	95.8	Ethers and alcohols: 107
7	$(C^2)^{II}-O$	-21.2	93.8	Disubstitutions
8	$(C^\phi)^{II}-O$	-20.6	93.2	Disubstitutions
9	C^2-O^{II}	-17.0	89.6	Ethers and alcohols
10	C^1-O^{II}	-18.8	91.5	Ethers and alcohols: 26, 29, 30, 70, 83, 84
11	C^0-O^{II}	-19.5	92.2	Refs. 27 and 79
12	$C^\phi-O(CO)$	-17.0	89.6	Aryl esters
13	$[(O)C^2]^{II}-O$	-21.2	93.8	Anhydride oxygen bridge, same value as term No. 7 above

14	$(O)C^2-O$	-28.8	101.4	The "short" bond in acids and esters
15	$C^2=O$	-22.3	167.5	The "carbonyl" in ketones and aldehydes
16	$(O)C^2=O$	-33.3	178.5	The "carboxyl" in acids, esters, acid halides, and anhydrides
17	$C^2=O$	-36.4	181.6	Ketene/carbon suboxide
18	$(OO)C^2=O$	-36.4	181.6	The "carboxyl" in carbonates
19	$C^2=O''$	-42.0	187.2	Carbon dioxide
20	$C^1 \equiv O$	-36.0	197.7	Carbon monoxide
21	$(O)C^2-H''$	-1.8	96.7	Formaldehyde
22	$(O)C^2-H$	-2.5	97.4	Aldehydes, formic acid
23	$(OO)C^2-H$	-2.5	88.1	Malonic acid
24	$[(OO)C^1]''-C^2$	-11.6	97.2	Vinyl ketones, acrylic and methacrylic acids and esters, etc.
25	$(O)C^2-C^\phi$	-10.0	95.6	Aromatic ketones, aldehydes, acids, esters, acid halides
26	$(OO)C^2-C^\phi$	-9.5	95.1	Benzoquinone
27	$(O)C^2-(C^2)''$	-8.2	93.9	Benzophenone

(continued)

TABLE 2 (continued)

No.	Bond ^a	ΔH_f° (g) (kcal/mole)	Bond strength (E_{25}°), (kcal/mole)	Compounds from which derived: references
(1)	(2)	(3)	(4)	(5)
28	(ϕ)-[C ² (OO)]''	(-11.3) \pm 3	96.9	Benzene polycarboxylic acids
29	C ² =C ²)-[C ² (OO)]''	(-5.6) \pm 3	91.2	Maleic, fumaric, citraconic acids and their esters
30	(O)C ² -C ² (O)	-3.6	89.2	Diacetyl, benzil
31	(OO)C ² -C ² (OO)	(+4.5) \pm 3	81.1	Oxalic acid, its acid chloride and esters
32	C ¹ -C ² (OO)	-8.0	93.6	Acetylene dicarboxylic acid
33	(O)C ² -F''	-59.8	118.1	Carbonyl fluoride
34	(O)C ² -F	-58.3	116.6	Acetyl fluoride
35	(O)C ² -Cl''	-9.6	81.4	Phosgene
36	(O)C ² -Cl	-8.0	79.8	Acyl/aroyl chlorides
37	(O)C ² -Br''	+3.1	66.5	Carbonyl bromide
38	(O)C ² -Br	+1.8	67.8	Acid bromides
39	(O)C ² -I	+15.7	52.6	Acid iodides
40	O-H''	-29.9	110.8	Water, peracids, hydroperoxides
41	(C)O-H	-26.4	108.3	Alcohols, phenols, carboxylic acids

42	O—F	+26.1	48.9	Oxygen fluoride
43	O—Cl	+24.2	63.3	Chlorine monoxide
44	(H)O—O(H)	+25.2	34.4	Hydrogen peroxide
45	(C)O—O(H)	+19.4	40.2	Alkyl/aryl hydroperoxides
46	(OC)O—O(H)	+18.4	41.2	Peracids and peresters
47	(C)O—O(C)	+13.5	46.1	Alkyl/aryl peroxides
48	(OC)O—O(CO)	+24.0	35.6	Acy/aroyl peroxides
49	(OOC)O—O(COO)	+33.8	25.8	Peroxydicarbonate
50	O=O	0.0	59.6	Oxygen (reference state)

Group Contributions

CHO (aldehyde), -24.8; COOH (acid), -88.5; OC(O)O (carbonate), -94.0; OCOCO (anhydride), -109.0; OH, 26.4 kcal/mole. Group contributions may be used, for convenience.

Ring Strain and Ortho-Correction Terms

51	Cyclo[C ² C ³ O] ₃	= (27.4 + 13.3 n - x - m) ± 1.5 kcal/mole		
52	Cyclo[C ² C ³ O] ₄	= (26.4 + 1.9 n - x - m) ± 2 kcal/mole		
53	Cyclo[C ² C ³ O] ₅	= (6.0 - x - m) ± 1 kcal/mole		
54	Cyclo[C ² C ³ O] ₆	= (0.0) ± 1 kcal/mole		
55	Cyclo[C ² C ³ O] _{7,9,9}	= strain unpredictable, but rarely exceeding 6 kcal/mole if only one single oxygen is present in the ring.		

(continued)

TABLE 2 (continued)

56	Cyclo[C ² C ³ O] _{10,11,12} = (3.0) ± 3 kcal/mole
57	Cyclo[C C ³ O] _{>12} = essentially strain-free, where n = number of C ² (other than exo-C ² in the case of 4 membered rings) x = 1, for single O, otherwise x = 0 m = number of substituted C ² or C ³ ring atoms (exo-C ² is taken as substituted C ²)
58	Ortho[C ² (OO), C ² (OO)] = 8.0 kcal/mole derived from phthalic acid, acid halide, and esters

TABLE 3. Some Recent Data on Oxygen Compounds (1969-1973) Tested by the Bond-Energy Scheme (This Work) and Group-Contribution Method [3]

No.	Compound	$\Delta H_f^\circ(\text{g})$ (obsd.), ^a (kcal/mole)	$\Delta H_f^\circ(\text{g})$ (pred., this work), ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
<u>(a) Alcohols</u>						
1	Methanol	-48.0	-48.2	+0.2	0.0	3, 11
2	Ethanol	-56.2	-56.3	+0.1	-0.1	3, 11
3	1-Propanol	-61.1	-61.2	+0.1	-0.1	3, 12
4	Methanediol	-93.5	-92.2	-1.3	-1.6	3, 13
5	1,1-Ethanedial	-103.1	-102.2	-0.9	-0.9	3, 14
6	Ethylene glycol	-92.7	-92.1	-0.6	-0.7	3, 21
7	1,2-Propanediol (+,-)	-100.7	-100.8	+0.1	+0.5	3, 21
8	1,3-Propanediol	(-93.7) ^c	-97.0	(+3.3) ^b	(+3.3) ^b	3, 21
9	1,3-Butanediol (+,-)	(-103.5) ^c	-105.7	(+2.2)	(+2.7)	3, 21
10	2,2-Dimethylpropan-1,3-diol	-131.7(c)	-109.9	(21.8) ^e	-	3, 21

(continued)

TABLE 3 (continued)

No.	Compound	ΔH_f° (g) (obsd.), ^a (kcal/mole)	ΔH_f° (g) (pred., this work), ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
11	1,4-Butanediol	-102.0	-101.9	-0.1	-0.1	3, 21
12	1,5-Pentanediol	-107.3	-106.8	-0.5	-0.4	3, 21
13	1,6-Hexanediol	-110.2	-111.7	+1.5	+1.6	3, 21
14	Resorcinol	-65.7	-65.0	-0.7	-1.3	3, 15
15	1-Butanol	-65.8	-66.1	+0.3	+0.2	3, 16
16	1-Pentanol	-70.7	-71.0	+0.3	+0.3	3, 16
17	1-Octanol	-85.3	-85.7	+0.4	+0.5	3, 16
18	1-Hexadecanol	-123.7	-125.0	+1.3	+1.7	3, 16
19	3,3,3-Trifluoropropanol	-229.4(1)	-216.0	(13.4) ^d	-	17
20	2,2,3,3-Tetrafluoropropanol	-263.3(1)	-251.4	(11.9) ^d	-	17
21	2,2,3,3,4-Pentafluoropropanol	-319.9(1)	-308.2	(11.7) ^d	-	17
22	2,2,2-Trifluoroethanol	-220.6(1)	-211.1	(9.5) ^d	-	18

23	1,1-Dihydroperfluorobutanol	-409.9(1)	-405.0	(15.5) ^d	-	19
24	$\text{HO}(\text{CH}_2)_2-(\text{CH}_2)_n-\text{C}(\text{CH}_2)_2\text{OH}$ (n = 2)	-169.2(1) ^c	-136.4	(?) ^d	-	20
25	$\text{HO}(\text{CH}_2)_2-(\text{CH}_2)_n-\text{C}(\text{CH}_2)_2\text{OH}$ (n = 3)	-181.9(1) ^c	-141.3	(?) ^d	-	20
26	$\text{HO}(\text{CH}_2)_2-(\text{CH}_2)_n-\text{C}(\text{CH}_2)_2\text{OH}$ (n = 4)	-184.5(1) ^c	-146.3	(?) ^d	-	20
27	$\text{HO}(\text{CH}_2)_2-(\text{CH}_2)_n-\text{C}(\text{CH}_2)_2\text{OH}$ (n = 6)	-188.7(1) ^c	-156.1	(?) ^d	-	20
28	$\text{HO}(\text{CH}_2)_2-(\text{CH}_2)_n-\text{C}(\text{CH}_2)_2\text{OH}$ (n = 7)	-199.8(1) ^c	-161.0	(?) ^d	-	20
29	$\text{HO}(\text{CH}_2)_2-(\text{CH}_2)_n-\text{C}(\text{CH}_2)_2\text{OH}$ (n = 8)	-202.2(1) ^c	-165.9	(?) ^d	-	20
(b) Ethers						
30	Methyl-n-propyl ether	-56.8	-56.6	-0.2	-0.4	3, 22
31	Methyl-isopropyl ether	-60.2	-60.4	+0.2	-0.1	3, 22
32	Di-n-butyl ether	-79.8	-79.3	-0.5	-0.5	3, 23
33	Di-s-butyl ether	-86.3	-86.6	+0.3	+0.6	3, 23
34	2-Methoxy-n-but-2-ene	(-39.9)	-42.4	(+2.5)	(+1.0)	3, 24
35	2-Ethoxy-prop-1-ene	-43.4	-42.7	-0.7	-1.2	3, 24
36	Diethyl ether	-59.8	-59.7	-0.1	-0.2	3, 29
37	Diphenyl ether	10.1	-	-	0.0	3
		11.9	12.0	+0.1	-	2

(continued)

TABLE 3 (continued)

No.	Compound	ΔH_f° (g) (obsd.) ^a (kcal/mole)	ΔH_f° (g) (pred., this work) ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
38	Dimethoxymethane	-83.2	-83.0	-0.2	-0.5	3, 26
39	1,1-Dimethoxyethane	-93.1	-93.1	0.0	-0.2	3, 26
40	2,2-Dimethoxypropane	-102.9	-102.7	-0.2	+2.4	3, 27
41	2,2-Diethoxypropane	-120.2	-118.7	-1.5	-0.7	3, 27
42	3,5-Dioxaheptane	-99.1	-99.1	0.0	-0.3	3, 28
43	3,6-Dioxaoctane	-97.6	-99.0	+1.4	+1.4	3, 28
44	3,5,7-Trioxanonane	-138.9	-139.3	+0.4	-0.7	3, 28
45	3,5,7,9-Tetraxaundecane	-177.1	-177.8	+0.7	+0.4	3, 28
46	3,5,7,9,11-Pentaaxatridecane	-216.5	-217.1	+0.6	+0.3	3, 28
47	1,1-Diethoxyethane	-108.4	-107.5	-0.9	+0.8	3, 29
48	Di-n-butoxymethane	-119.8	-118.7	-1.1	-1.1	3, 2
49	2,4,6-Trimethyl-3,5-dioxaheptane	-125.7	-126.5	+0.8	+0.7	3, 30
50	6-Ethyl-5,7-dioxaundecane	-132.1	-132.5	+0.4	+1.8	3, 30
51	Methyl- α -chloroethyl ether	-65.2	-64.5	-0.7	-	31

52	Methyl iodomethyl ether	-29.3	-29.8	+0.5	-	31
53	Methyl vinyl ether	-26.2	-25.5	-0.7	-	31
54	1,3-Diethoxypropane	-104.3	-103.9	-0.4	-	32
55	Glycidyl-t-butyl ether	-88.5(1)	-80.2	(8.3) ^d	-	33
56	Glycidyl-2-methylbutyl ether	-93.8(1)	-85.1	(8.7) ^d	-	33
57	Glycidyl-2-methylhexyl ether	-105.7(1)	-95.1	(10.6) ^d	-	33
58	Anisole (phenyl methyl ether)	-17.3	-18.4	+1.1	-	2
		-19.6	-18.4	-1.2	-	38
<u>(c) Aldehydes and Ketones</u>						
59	Formaldehyde	-26.0	-25.9	-0.1	0.0	3, 34
60	Acetaldehyde	-39.7	-39.6	-0.1	-0.5	2, 3
61	Propionaldehyde	-44.5	-44.6	+0.1	-0.1	3, 12
62	Octanal	(-66.8) ^c	-64.2	(+2.6)	(+2.3)	3, 40
63	Acrolein	-17.8	-16.8	-1.0	0.0	3, 36
64	But-2-enal	-25.5	-24.6	+0.6	+0.1	3,
		-24.0	-24.6	+0.6	-	2
65	Benzaldehyde	-8.9	-8.2	+0.2	0.0	3
		-8.0	-8.2	+0.2	-	38, 80

(continued)

TABLE 3 (continued)

No.	Compound	ΔH_f° (g) (obsd.), ^a (kcal/mole)	ΔH_f° (g) (pred., this work), ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
66	Glyoxal	-50.6	-51.8	+1.1	0.0	3, 34
67	Methylglyoxal	-64.8	-64.8	0.0	-0.2	2, 3
68	Diethyl ketone	-61.7	-61.8	+0.1	+0.3	3, 39
69	Methyl-n-propyl ketone	-61.9	-61.8	-0.1	-0.2	3, 39
70	Methyl isopropyl ketone	-62.8	-63.3	+0.5	+0.6	3, 39
71	Methyl n-butyl ketone	-66.9	-66.7	-0.2	-0.2	3, 39
72	Methyl t-butyl ketone	-69.5	-69.6	+0.1	+0.8	3, 39
73	Ethyl n-propyl ketone	-66.5	-66.7	+0.2	+0.4	3, 39
74	Ethyl isopropyl ketone	-68.4	-68.2	-0.2	+0.1	3, 40
75	Ethyl t-butyl ketone	-75.0	-74.5	-0.5	+0.5	3, 40
76	Diisopropyl ketone	-74.4	-74.6	+0.2	+0.7	3, 40
77	Isopropyl t-butyl ketone	-80.8	(-79.2) ^f	-1.6	(+1.3) ^f	3, 40
78	Di-n-butyl ketone	-82.4	-81.4	-1.0	-0.6	3, 39

79	Di- <i>t</i> -butyl ketone	-82.6	(-82.0) ^f	-0.6	(+6.5) ^f	3, 40
80	Methyl hexyl ketone	(-82.5) ^c	-76.5	(-6.0)	(-5.9)	3, 41
81	Ethyl pentyl ketone	(-80.9) ^c	-76.5	(-4.4)	(-4.1)	3, 41
82	Propyl butyl ketone	(-83.5) ^c	-76.5	(-7.0)	(-6.7)	3, 41
83	Diisobutyl ketone	-85.5	-84.1	-1.4	-1.2	3, 40
84	<i>t</i> -Butyl neopentyl ketone	-94.2	-93.2	-1.2	-0.5	3, 40
85	Di- <i>n</i> -pentyl ketone	-92.6	-91.3	-1.3	-0.9	3, 39
86	Acetyl acetone, enol	-79.1	-78.8	-0.3	-	42
	Diacetyl, keto	-77.2	-77.9	+0.7	-	42
87	Methyl- α -iodoethyl ketone	-38.2	-35.0	(-3.2)	-	43
88	Ketene	-11.4	-11.2	-0.2	-	45
89	2, 2, 6, 6-Tetramethyl-4-heptanone	-100.7	-99.2	-1.5	-	46
90	3-Methylpentan-2-one	-67.9	-68.1	+0.2	-	47
91	4-Methylpentan-2-one	-69.6	-68.1	-1.5	-	47
92	Heptan-4-one	-71.3	-71.6	+0.3	-	47
93	3,3-Dimethylpentan-2-one	-72.6	-73.8	+1.2	-	47
94	4,4-Dimethylpentan-2-one	-76.6	-75.6	-1.0	-	47
95	3,3,4-Trimethylpentan-2-one	-78.5	-77.7	-0.8	-	47

(continued)

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(g)$ (obsd.), ^a (kcal/mole)	$\Delta H_f^\circ(g)$ (pred., this work), ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
96	3,3,4,4-Tetramethylpentan-2-one	-83.1	-83.1	0.0	-	47
97	Perfluoroacetone	-325.2 (at 600 K)	-354.9	-	-	48
(d) Acids, Esters, Acid Halides, Anhydrides, and Carbonates						
98	Formic acid	-90.5	-91.0	+0.5	-0.3	3, 49
99	Maleic acid	-162.4	-161.6	-0.8	(+6.8) ^g	2, 3
100	Fumaric acid	-161.3	-161.6	+0.3	(+8.9) ^g	2, 3
101	Benzoic acid	-70.1	-	-	(+4.4)	3
		-71.1	-71.9	+0.8	-	50, 51
102	Phthalic acid	-186.9(c)	-158.2	(-28.7) ^e	-	2, 51
103	Isophthalic acid	-191.9(c)	-166.2	(-24.7) ^e	-	51
104	Terephthalic acid	-195.1(c)	-166.2	(-28.9) ^e	-	51

105	Hemimellitic acid	-277.3(c)	-243.2	(-34.1) ^e	-	51
106	Trimellitic acid	-281.8(c)	-251.2	(-30.0) ^e	-	51
107	Trimesic acid	-284.5(c)	-259.2	(-25.3) ^e	-	51
108	Prehnitic acid	-370.1(c)	-328.2	(-41.9) ^e	-	51
109	Mellyphanic acid	-373.4(c)	-336.2	(-37.2) ^e	-	51
110	Pyromellitic acid	-375.4(c)	-336.2	(-39.2) ^e	-	51
111	Benzenepentacarboxylic acid	-461.2(c)	-413.2	(-48.0) ^e	-	51
112	Mellitic acid	-549.4(c)	-490.2	(-59.2) ^e	-	51
113	Acetic anhydride	-137.1	-138.7	+1.6	-0.2	2, 3
114	Propionic anhydride	-149.7	-148.5	-1.2	-2.4	2, 3
115	Benzoic anhydride	-76.3	-75.8	-0.5	-0.6	3, 52
		-79.9				3
116	Methyl formate	-85.0	-86.4	+1.4	+0.3	3, 53
117	Ethyl propionate	-110.8	-111.7	+0.9	+0.9	3, 54
118	Methyl methacrylate	-81.5	-	-	0.0	3
		-84.2	-85.1	+0.9	-	9
119	Methyl- α -methyl butyrate	(-117.7) ^c	-114.9	(-2.8)	(-3.4)	3, 56

(continued)

TABLE 3 (continued)

No.	Compound	ΔH_f° (g) (obsd.) ^a (kcal/mole)	ΔH_f° (g) (pred., this work) ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
120	Ethyl- α -methyl butyrate	(-124.9) ^c	-122.9	(-2.0)	(-2.5)	3, 56
121	Methyl isovalerate	(-119.9) ^c	-114.9	(-5.0)	(-5.1)	3, 56
122	Ethyl isovalerate	(-126.0) ^c	-122.9	(-3.1)	(-3.2)	3, 56
123	Methyl pivalate	(-122.8) ^c	-116.4	(-6.4)	(-5.7)	3, 56
124	Diethyl oxalate	(-177.3) ^c	-179.4	(+2.1)	(+3.9)	3, 57
125	Diphenyl oxalate	(-104.5) ^c	-100.5	(-4.0)	(-3.9)	3, 41
126	Diethyl fumarate	-174.7	-168.5	(-6.2)	(+1.9)	3, 58
127	Phenyl benzoate	-34.0			+3.5	3, 52
		-36.2	-35.9	-0.3	-	61
		-37.5				3, 60
128	Phenyl acetate	-64.6	-67.3	+1.7	-	38
		-67.0	-67.3	-0.7	-	2

129	Ethyl acetate	-106.8	-106.8	0.0	-	62
130	Isopropyl acetate	(-116.1)	-115.5	0.6	-	2, 62
131	Diethyl carbonate	-152.5	-153.7	+1.2	-	3, 54
		(-163.5) ^c	-	-	-	63
132	Methylcyclohexyl carbonate	-158.5	-158.5	[0.0] ^h	-	61
133	Dicyclohexyl carbonate	(-182.6)	-179.4	(3.2)	-	61
134	Di(p-phenylbenzyl)carbonate	(-50.0) ^c	-44.0	(-6.0)	-	63
135	Diphenyl carbonate	-74.4	-73.6	-0.8	-	52
136	Benzoyl peroxide	-67.0	-67.0	[0.0] ^h	-	61
137	o'-Cyclohexyl-o-benzoyl peroxycarbonate	-154.0	-155.5	+1.5	-	61
138	o-Phenyl-o-benzoyl peroxycarbonate	-93.9	-101.9	(+8.0)	-	61
139	Dicyclohexylperoxy dicarbonate	-239.6	-239.6	[0.0] ^h	-	61
140	Cumyl peroxybenzoate	-45.0	-40.6	(-4.4)	-	61
141	Benzoyl bromide	2.6	1.0	+1.6	-	37
142	Benzoyl chloride	-24.7	-24.7	0.0	-	65
143	Carbonyl bromide	-27.1	-27.1	[0.0] ^h	-	66

(continued)

TABLE 3 (continued)

No.	Compound	$\Delta H_f^\circ(\text{g})$ (obsd.), ^a (kcal/mole)	$\Delta H_f^\circ(\text{g})$ (pred., this work), ^a (kcal/mole)	Error (obsd. - pred.) ^a		Refs.
				This work (kcal/mole)	Ref. 3 (kcal/mole)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
144	Phosgene	-52.6	-52.5	-0.1	-	67
		-52.4	-52.5	+0.1	-	68, 69
145	Carbon tetrachloride	-28.0	(-28.0)	[0.0] ^{h,i}	-	69
				Overall Standard Deviation:	± 0.83	± 0.91

^aSee footnotes a to d of Table 5.

^bParenthesized values in these columns have been excluded throughout from the overall standard deviation at the end.

^cThe experimental value appears to be seriously in error and needs reexamination.

^dThe heat of vaporization is predicted in the absence of the experimental value.

^eThe heat of sublimation is predicted.

^fThe steric strain due to 1-3 interaction of the bulky t-butyl group has been treated by special terms for hydrocarbons taken from earlier work [1b]; the group-contribution scheme [3] does not provide for such special steric effect, hence the large deviation.

^gThe effect of multiple substitution of -COOH in a resonant structure is not recognized by the group-contribution scheme [3], hence the large error.

^hExcluded from the overall standard deviation since the (zero) value originates in the unique datum and the energy term derived thereof.

ⁱThe new precise experimental value of $H_f^\circ(\text{g})$ of carbon tetrachloride [69] calls for a revision of the earlier bond energy term $\text{C}^3-\text{Cl}^{\text{IV}}$ in our previous paper [1d].

Multiple substitutions of C^2 or C^1 on a resonating structure (ethylene, benzene, etc.) call for a reasonable average energy term for the bond $C^2-(R)$. This average value may be lower or higher than the value for the single substitution, depending upon the extent of delocalization as well as the total resonance "capacity" of the conjugated structure. This value of -10.0 kcal/mole for the $(O)C^2-C^\phi$ bond in benzoic acid increased to -11.3 for the same bond (as average value) in benzene-polycarboxylic acids, such as isophthalic acid, but similar disubstitution of $-COOH$ in ethylene caused a substantial reduction in the average strength of the $(O)C^2-C^2$ bond in maleic or fumaric acids, viz., term No. 29 as against No. 24 in Table 2. Since the maximum resonance capacity of such structures as benzene or ethylene is not precisely known at present due to lack of complete thermochemical data, the bond energy terms offered in the present scheme are limited to the first two or at the most three identical substitutions in a conjugated structure.



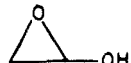



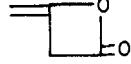

In peroxy compounds, six different values for the $O-O$ bond were identified which depended upon inductive association of either of the two oxygen atoms with various groups, viz., the hydrogen atom (hydrogen peroxide, hydroperoxides, and peracids), the alkyl or aryl group, the acyl or aroyl group, or the carbonate group. These relate to terms Nos. 44 to 49 in Table 2. Combinations other than those mentioned under these energy terms may be worked out (reasonably) by simple averaging of the respective $O-O$ bond energy terms. The energy term for the $O-O$ link between two carbonates has been derived from a singular value of the peroxy-dicarbonate [61].

About 10 bond energy terms in Table 2, shown by an underlined serial number, are unique in that these have been derived from a singular specific compound and applicable only to the same compound; for instance, the $C^2=O$ bond in carbon dioxide, the $O-H$ in water, and the C^1-O in carbon monoxide. These terms have been listed for the purpose of comparison and correlation with similar bonds in oxygen compounds. Such unique compounds are to be noted as specific exceptions to the bond-additivity principle. The $O-H$ bond of water has, however, been found applicable as a common bond for hydroperoxides and peracids.

STRAIN ENERGY AND RESONANCE ENERGY

Cyclic oxygen compounds, associated with strain energy and occasionally resonance energy whenever C^2 or C^1 carbons form ring members, are listed in Table 4, together with the simplified structural formula and the experimental enthalpies of formation. Column 5 of Table 4 gives the basic bond-energy contribution, which does not take into consideration the strain energy (E_s) or the resonance (binding) energy (E_b) in the molecular structure.

TABLE 4. Cyclic Oxygen Compounds Correlated by the Bond-Energy Binding Energy (E_b)

No.	Compound	Structure ^a
(1)	(2)	(3)
<u>3-Membered Rings</u>		
1	Ethylene oxide	
2	Propylene oxide	
3	2,3-Epoxy-1-propanol	
<u>4-Membered Rings</u>		
4	Trimethylene oxide ("oxetane")	
5	Cyclobutanone	
6	β -Propiolactone	
7	Diketene	
8	Dihydrocyclobutenedione ("squaric acid")	

Scheme and Estimation of the Strain Energy (E_s) or the Excess

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-12.6 ± 0.2	-39.3	+26.7	-12.9	+0.3	2
-22.6 ± 0.2	-48.0	+25.4	-22.6	0.0	2
-58.0 ± 1.0	-83.8	+25.8	-58.4	+0.4	2, 6a
-19.2 ± 0.2	-44.2	+25.0	-18.8	-0.4	2, 3
-24.2 ± 0.3	-46.3	[+22.1]	-20.9	(-3.3)	3, 49
-67.6 ± 0.2	-91.3	+23.7	-66.9	-0.7	3, 73
-45.5 ± 0.2	-72.2	[+26.7]	-48.9	(+3.4)	3, 71
-123.0 ± 0.2	-132.6	[+9.6]	-106.4	(-16.6)	74

(continued)

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
9	Diethoxycyclobutenedione	
10	Phenylcyclobutenedione	
11	3,3-Dimethyl oxetane	
12	3-Ethyl-3-chloromethyloxetane	
13	3,3-bis-Chloromethyl oxetane	
14	Tetramethyl-1,3-cyclobutane-1,3-dione	
<u>5-Membered Rings</u>		
15	Furan	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-114.4 ± 2.0	-139.5	+25.1	-113.3	-1.1	74
-7.1 ± 1.0	-23.2	[+16.1]	4.0	(-11.1)	74
-35.4 ± 0.4	-58.8	+23.4	-34.4	-1.0	75
-46.2 ± 0.4	-71.2	+25.0	-46.8	+0.6	75
-48.8 ± 0.5	-73.8	+25.0	-49.4	+0.6	75
-73.5 ± 0.4	-94.6	+21.1	-72.2	-1.3	76
-8.3 ± 0.2	-2.1	[-6.2]	2.9	(-11.2)	2, 3

(continued)

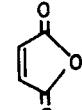
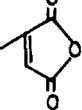




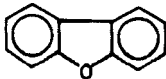
TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
16	2-Methyl-4,5-dihydrofuran	
17	Tetrahydrofuran	
18	Cyclopentanone (keto)	
	(enol)	
19	Succinic anhydride	
20	1,1-Dimethylsuccinic anhydride	
21	Trimethylsuccinic anhydride	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-31.1	-34.9	+3.8	-30.9	-0.2	3, 77
-44.0 ± 0.2	-49.1	+5.1	-44.1	+0.1	3, 78
-46.6 ± 0.4	-51.2	+4.6	-46.2	-0.4	3, 49
	-41.3		-36.3		c
-122.6 ± 0.5	-128.1	+5.5	-125.1	+2.5	2, 3
-139.0 ± 0.6	-140.8	+1.8	-138.8	-0.2	2, 3
-146.8 ± 0.6	-147.2	+0.4	-146.2	-0.6	2, 3

(continued)

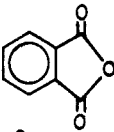
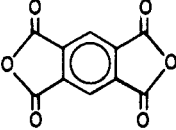
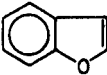
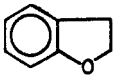
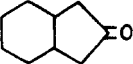
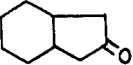

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
22	Maleic anhydride	
23	Methylmaleic anhydride	
24	Furfuryl alcohol	
25	Furfural	
26	Tetrahydrofurfuryl alcohol	
27	Cyclopentanol	
28	Dibenzofuran	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-96.9 ± 1.0	-93.6	[-3.3]	-90.6	(-6.3)	3, 55
-106.9 ± 1.0	-102.7	[-4.2]	-100.7	(-6.2)	2, 3
-50.6 ± 0.5	-46.0	[-4.6]	-42.0	(-8.6)	2, 3
-36.1 ± 1.2	-32.8	[-3.3]	-28.8	(-7.3)	2
-88.2 ± 1.5	-93.2	+6.8	-89.2	-1.0	2, 3
-58.0 ± 0.3	-64.2	+6.2	-59.2	+1.2	2
19.9 ± 1.2	14.9	+5.0	19.9	0.0	2, 3

(continued)

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
29	Phthalic anhydride	
30	Pyromellitic anhydride	
31	Benzofuran ("coumarone")	
32	Dihydrobenzofuran	
33	Hydrindanone, cis	
34	Hydrindanone, trans	
35	8-Methyl-1,2-hydrindanone, cis	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-88.8 ± 0.5	-98.2	[+9.4]	-	-	3
-196.9 ± 1.0	-216.2	[+19.3]	-	-	3
	+7.5	-	-12.5	-	c
	-18.4	-	-13.4	-	c
-59.7 ± 0.3	-63.2	+3.5	-60.2	+0.5	81
-59.6 ± 0.4	-63.2	+3.6	-60.2	+0.6	81
-68.6 ± 0.8	-71.4	+2.8	-68.4	-0.2	82

(continued)

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
36	8-Methyl-1,2-hydrindanone, trans	
37	Ethylene carbonate	
38	Propylene carbonate	
39	Vinylene carbonate	
40	1,3-Dioxolane	
41	2-Methyl-1,3-dioxolane	
42	2,4-Dimethyl-1,3-dioxolane, cis	
43	trans	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-65.8 ± 0.6	-71.4	[+5.6]	-68.4	(+2.6)	82
$(-120.3) \pm 0.5$	-133.3	[+13.0]	-128.3	-	63, 64
-139.3 ± 0.5	-142.0	+2.7	-138.0	-1.3	63, 64
(-100.6 ± 2.0)	-113.9	[+13.2]	-108.8	(+18.2)	63
-72.1 ± 0.5	-78.6	+6.5	-72.6	+0.5	3, 83
-84.1 ± 0.7	-88.6	+4.5	-83.6	-0.5	3, 83
-91.5 ± 0.9	-97.4	+5.9	-93.4	+1.9	3, 83
-91.0 ± 0.9	-97.4	[+6.4]	-93.4	(+2.4)	3, 83

(continued)

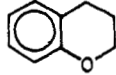
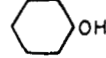
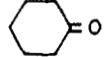
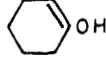


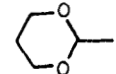

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
44	1,3-Dioxindane	
45	Cyclopentadienone	
46	Dioxole	
47	2,4-Dimethyl-1,3-dioxole	
<u>6-Membered Rings</u>		
48	Dihydropyran	
49	Tetrahydropyran	
50	2-Methoxytetrahydropyran	
51	Dibenzopyran	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-34.1 ± 0.8	-52.4	[+18.3]	-46.4	(+12.3)	2, 3
	-1.0	-	+4.0	-	c
	-59.1	--	-53.1	-	c
-83.7 ± 0.8	-78.3	[-5.4]	-74.3	(-9.4)	85
-29.9 ± 0.4	-30.6	+0.7	-30.6	+0.7	3, 25
-53.4 ± 0.3	-54.0	+0.6	-54.0	+0.6	2, 3
-95.5 ± 0.5	-95.4	-0.1	-95.4	-0.1	2, 3
11.6 ± 1.2	11.8	-0.2	11.8	-0.2	2, 3

(continued)

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
52	Benzopyran	
53	Cyclohexanol	
54	Cyclohexanone, keto enol	
		
55	p-Benzoquinone	
56	1,3-Dioxane	
57	2-Methyl-1,3-dioxane	
58	4-Methyl-1,3-dioxane	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
	4.2		4.2	-	c
-68.4 ± 0.4	-69.1	+0.7	-69.1	+0.7	2, 3
-54.4 ± 0.5	-56.1	+1.7	-56.1	+1.7	3, 49
	-46.2		-46.2	-	c
-29.3 ± 0.9	-29.3	0.0	-29.3	0.0	2
-83.4 ± 0.3	-83.5	-0.1	-83.5	-0.1	3, 84
-94.8 ± 0.4	-93.6	-1.2	-93.6	-1.2	3, 84
-92.6 ± 0.4	-92.3	-0.3	-92.3	-0.3	3, 84

(continued)

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
59	cis-2,4-Dimethyl-1,3-dioxane	
60	trans-4,5-Dimethyl-1,3-dioxane	
61	5,5-Dimethyl-1,3-dioxane	
62	2,2,4-Trimethyl-1,3-dioxane	
63	2-cis,4-trans,6-trimethyl-1,3-dioxane	
64	2,2,4,6-Tetramethyl-1,3-dioxane, trans	
65	2,2,4,6-Tetramethyl-1,3-dioxane, cis	
66	1,4-Dioxane	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-102.3 ± 0.5	-102.3	-0.0	-102.3	0.0	2, 70
-98.2 ± 0.4	-98.7	+0.5	-98.7	+0.5	2, 70
(-100.7 ± 0.4)	-98.2	-2.5	-98.2	-2.5	2, 70
-110.1 ± 0.5	-111.9	+1.8	-111.9	+1.8	3, 79
-106.8 ± 0.5	-111.0	[+4.2]	-111.0	(+4.2)	3, 70
-116.0 ± 0.5	-120.6	[+4.6]	-	-	3, 79
-119.1 ± 0.5	-120.6	+1.5	-120.6	+1.5	3, 79
-79.9 ± 0.2	-78.5	-1.4	-78.5	-1.4	2, 3

(continued)

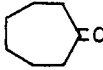
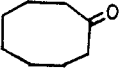

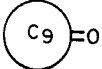




TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
67	1,4-Dioxatetralin	
68	sym-Trioxane	
69	2,4,6-Trimethyltrioxane ("paraldehyde")	
70	Cyclohexatrienone, keto	
	enol	
	Phloroglucinol (resonant)	
<u>7-Membered and Large Rings</u>		
71	Tropolone	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-48.8 ± 0.8	-52.3	[+3.5]	-52.3	(+3.5)	2, 3
-111.3 ± 0.2	-118.1	[+6.8]	-118.1	-	3, 72
-153.1 ± 0.5	-148.1	[-5.0]	-	-	3, 86
-	-109.4	(?)	-109.4	-	c
-	-90.8	(?)	-	-	
-151.6(c)	-108.6	(?)	-108.6	-	90 ^c
-37.2 ± 0.3	12.7 (carbonyl)	[-49.9]	-	-	87
	-1.4 (carboxyl)	[-35.8]	-	-	

(continued)




TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
72	Cycloheptanone ("troponone")	
73	Cyclooctanone	
74	sym-Tetroxane	
75	Cyclononanone	
76	Cyclodecanone	
77	Cycloundecanone	
78	Cyclododecanone	
79	Cyclopentadecanone	

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-59.3 ± 0.3	-61.0	[+1.7]	-	-	3, 49
-65.0 ± 0.4	-65.9	[+0.9]	-	-	3, 49
-148.2 ± 0.2	-157.4	[+9.2]	-	-	3, 72
-66.8 ± 0.4	-70.8	[+4.0]	-	-	3, 40
-72.9 ± 0.5	-75.7	[+2.8]	-	-	3, 49
-77.0 ± 0.5	-80.6	[+3.6]	-	-	3, 49
-83.4 ± 0.6	-85.6	[+2.2]	-	-	3, 49
-99.1 ± 0.5	-100.3	[+1.2]	-	-	3, 49

(continued)

TABLE 4 (continued)

No.	Compound	Structure ^a
(1)	(2)	(3)
80	Cycloheptadecanone	
81	cis- β -Bicyclooctanone	
82	trans- β -Bicyclooctanone	

Standard Deviation (40 compounds):

^aSimplified structure; bond link (-) represents methyl or

^bRefer to footnotes a to d in Table 5.

^cPredicted value.

Column 6 gives the net balance of the strain energy over the resonance energy, i.e., $E_s - E_r$, a positive value indicating a net strain and a negative value an excess resonance energy after overcoming the strain inherent to the particular ring size. The resonance energy, being a specific property of the conjugated structure, is merely indicated as a parenthesized negative value in column 8 of the table. The strain energy, however, seems to be an additive and transferable property, at least for simple monocyclic molecules. Some simple empirical equations for computing the ring strain are proposed at the end of Table 2.

$\Delta H_f^\circ(g)$ (obsd.), ^b (kcal/mole)	Basic bond contribution (kcal/mole)	$(E_s - E_b)$ (kcal/ mole)	$\Delta H_f^\circ(g)$ (pred.), ^b (kcal/ mole)	Error/ correction (obsd. - pred.), (kcal/ mole)	Refs.
(4)	(5)	(6)	(7)	(8)	(9)
-110.0 ± 0.5	-110.1	[+0.1]	-	-	3, 49
-55.0 ± 1.3	-63.2	[+8.2]	-	-	2, 3
-49.4 ± 1.3	-63.2	[+13.8]	-	-	2, 3

experimental, ±0.7; bond-energy scheme, ±1.0

substituted methyl group.

Strain Energy Equation

Factors responsible for creating the ring strain have been discussed at length in Part III [1c]. The introduction of a single oxygen atom in small rings (3-, 4-, and 5-membered) reduces the strain by about 1 kcal/mole, which is primarily due to the removal of two hydrogens, thereby reducing nonbonded interactions (Pitzer strain), rather than being due to any significant change in the angular strain (Bayer strain). A similar reduction in nonbonded interactions is brought about by a methyl substitution on the member atom, and

also by introduction of a carbonyl C^2 or an $exo-C^2$ as a ring member. The second oxygen atom in the ring seems to cause angular strain that nullifies the strain relief gained in nonbonded interaction by removal of even 4 hydrogens. This restores the net strain approximately to its original value pertinent to the ring size. These factors, together with the terms earlier derived for angular strain in hydrocarbon rings, have been quantified in empirical equations Nos. 51 to 54 in Table 2. The strain in 6-membered ring is essentially zero and seldom changes beyond ± 1 kcal/mole for ordinary trivial changes in the ring composition. The ring strain in medium-sized rings (7- to 12-membered) is totally unpredictable and requires more elaborate computer-based calculations through conformational energy-minimization procedures as envisaged by Boyd and co-workers [104] and others [105]. Rings larger than 12-members may be freely assumed to be strain-free for the purpose of bond-energy or group-contribution methods. The last term in Table 2 deals with the strain, as high as 8 kcal/mole, caused by two carboxyl (COO) groups in the ortho position as in phthalic acid and its derivatives. Two such carbonyl (CO) groups, however, seem to produce lesser excess strain in phthalic anhydride over its normal value in a 5-membered ring. The excess strain due to ortho substitution in phthalic anhydride is only about 6.4 kcal/mole, as seen from item No. 29 in Table 4; that in pyromellitic anhydride is about double this value, as expected.

DISCUSSION

In the earlier work on hydrocarbons [1b], an approximately linear relationship between bond length and bond energy was envisaged for the C—C and C—H bonds. Such a simple relationship is, however, found inadequate for carbon bonds with a polar or polarizable heteroatom such as oxygen, nitrogen, or sulfur. A more satisfactory correlation was the modified Sutherland equation [4a]:

$$kr^2/E^\circ = S_{ij}, \quad \text{a constant}$$

where the bond dissociation energy D_e in the original form has been replaced by the thermochemical bond energy E° as a rational approximation [5], k is the equilibrium force constant, and r is the equilibrium bond/length. Table 1 presents the various parameters for the new bonds identified in this work. Column 3 gives the bond energies (E°) derived from $\Delta H_f^\circ(g)$, i.e., contributions of the bonds

and heats of atomization of the elements in their standard states [7]. The bond lengths in column 4, where shown to four significant figures, have been taken from microwave, electron, or x-ray diffraction work of recent origin on the key compounds in column 8; otherwise they are from the compilation of Sutton [102]. The literature source for the force constants in column 5 is Refs. 92-101. The parenthesized approximate values of force constants have been calculated from the assigned fundamental vibration frequency ν_{stretch} available from recent literature on interpreted IR and Raman spectral data of key compounds. It may be seen from S_{ij} in column 6 that the modified Sutherland relationship is obeyed fairly well by the new bonds assumed in this work. Except for hydrogen-halogen bonds, S_{ij} has shown a constant value, within small limits, for a typical bond between atoms i and j over a wide range of energies and bond lengths, as summarized in Table 1(H). Thus the Sutherland constants used in this table served as good guidelines for recognizing the different energies possessed by one single typical bond in different compounds; for instance, the $C^2=O$ bond in aldehydes, ketones, acids, acid halides, carbonates, etc. It is also seen from Table 1(H) that the Sutherland constant for homonuclear bonds between two strongly electronegative elements is high (24 to 27), that for all carbon bonds it is in the range 11 to 15, and for bonds with hydrogen it is in the range 3 to 7.

The scope and validity of the Sutherland-type correlation can be considerably enhanced if $S_{ij}/\sqrt{\mu}$ is used in place of S_{ij} as the new constant applicable to any type of bond between atoms i and j , taking into account the reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$. The value of $S_{ij}/\sqrt{\mu}$ in the last column of Table 1(H) has a much narrower range of variation (only 4 to 6 in arbitrary units), except for the O—O bond in peroxides where the thermochemical data is perhaps not very precise. We shall revert to these empirical correlations with further consideration of electronegativity and its partial energy contribution to the covalent bond [35] at the end of this work (including nitrogen and sulfur compounds).

In order to test the success of the bond-energy procedure, recent data on 145 oxygen compounds have been treated in Table 3 and comparison made with the group-contribution procedure [3a]. It may be seen from columns 5 and 6 that both procedures are close and parallel in predicting $H_f^\circ(g)$, the overall standard deviation for the bond-energy procedure (± 0.8) being slightly better than for the group-contribution procedure (± 0.9), in spite of a much smaller number of energy terms in the former.

Alcohols

Most of the predicted heats of formation are within 1 kcal/mole of the measured values. The aliphatic monohydroxy alcohols are in even better agreement (± 0.5 kcal/mole). Some large discrepancies occur with polyols, and this might be attributed to hydrogen bonding. Where gas phase experimental values are not available, the predicted enthalpies of phase change are also seen to be reasonable, except for data on compounds Nos. 24 to 29 in Table 3. For this data and such other parenthesized experimental values, where both the schemes show almost the same discrepancy in magnitude and sign, we feel that a careful reexamination of the experimental work is warranted.

Ethers

Without serious exception, deviations no greater than ± 0.8 kcal/mole were observed, the average value being around ± 0.4 kcal/mole.

Aldehydes and Ketones

The overall deviation is about ± 1.0 kcal/mole. Severe departures in compounds Nos. 80, 81, 82, and 87 indicate that the experimental data may be in error.

Carboxylic Acids and Derivatives

Within this class of compounds more departures from bond additivity seem to occur than elsewhere. The experimental data from which our energy terms are derived are scanty and generally date back to 1940 or earlier. The data are often based on reactions other than combustion and are arbitrarily extrapolated to the standard state. The enthalpies of phase change (generally sublimation) have not been measured or confirmed to a uniquely/unambiguous value. Benzoic acid is a prominent example of where the heat of sublimation was doubtful until the recent work of Malaspina et al. [50]. The experimental data on acid halides and anhydrides are generally obtained from the heat of hydrolysis in solution. The experimental heats of combustion on some organic carbonates are conflicting [54, 63, 64]. However, the predicted values through our recommended energy terms may be found to be generally within ± 1.5 kcal/mole of good experimental data determined by modern thermochemical standards and techniques.

Cyclic Compounds

Cyclic oxygen compounds are listed in Table 4. Instead of giving strain energy correction terms for all individual rings as is done in the group-contribution scheme of Benson and co-workers [3], we have attempted, with fairly good success, to formulate simple empirical equations for various ring sizes by recognizing the most important structural factors responsible for the ring strain. These equations are given in the last section of Table 2 as terms Nos. 51 to 58. Most of the predicted heats of formation computed through these terms fall within ± 1.0 kcal/mole of the observed values. Larger deviations originating from specific structural feature and/or delocalization energy are shown as errors (parenthesized figures in column 8) which must be remembered as "exceptions" to the bond-additivity principle. Compounds Nos. 29, 30, 39, 44, 68, 74, 75, 81, and 82 are such special cases of ring strain, and compounds Nos. 8, 10, 15, 22-25, 47 and 69 are those where resonance energy predominated. As mentioned earlier, such compounds need advanced theoretical a priori treatment [104].

Monomers and Polymers

Systems Nos. 1-6 and 20-35 in Table 5 deal with the heats of formation and polymerization reaction through a double-bond opening at C=C or C=O unsaturation in the monomer molecule. Systems Nos. 7-19 and 46-47 represent polymerization through ring opening where the ring strain forms the main driving force for the reaction. The remaining systems in Table 5 represent polycondensation or polyesterification (elimination of H₂O, HCl, or other small molecule) and other reactions leading to polymer formation or polymer modification. The available experimental heats of polymerization (column 11) compare closely with the predicted values in the appropriate phases (columns 9 and 10). The hypothetical heat of vaporization of the polymer repeat segment has been computed by empirical methods [6, 10], whereby the $\Delta H_f^\circ(1)$ of polymers in the amorphous "liquid" state above the glass temperature have been derived as in column 8. It is hoped that the data of Table 5 will be helpful for a better theoretical interpretation of work on individual monomer-polymer systems and will also form a supplement to the author's earlier encyclopedic compilation [9].

The bond-energy scheme provides a valuable tool for calculating the heats of chemical reactions, even hypothetical reactions, of

TABLE 5. Heats of Formation, Polymerization, Polycondensation, Hydrolysis, etc. (25°C, kcal/mole) for

No.	Monomer	$\Delta H_f^\circ(x)$ (obsd.) ^f	$\Delta H_f^\circ(g)$ (pred.) ^g	$\Delta H_f^\circ(l)$ (calc.) ^h	Polymer structure (repeat unit)
(1)	(2)	(3)	(4)	(5)	(6)
1	Formaldehyde	-25.9(g)	-25.9	-31.0	...C-O...
2	Trioxane	-124.8(c'')	[-111.3]	-118.6	..COCOCO..
3	Tetraoxane	-167.3(c'')	[-148.2]	[-156.8]	..COCOCOCO..
4	Acetaldehyde	-39.7(g)	-39.6	-46.0	..CO.. C
5	Acetone	-51.9(g)	-52.0	-59.0	..CO.. C
6	n-Butyraldehyde	-48.9(g)	-49.5	-57.0	..CO.. C C C
7	Ethylene oxide	-12.6(g)	-12.9	-19.0	..CCO..
8	Tetramethyl ethylene oxide		-50.1	-61.8	..CCO.. CC
9	Epichlorohydrin		-30.1	-39.6	..CCO.. C Cl
10	Propylene oxide	-22.2(g)	-22.6	-29.3	..CCO.. C
11	3-Chloropropylene oxide		-33.6	-42.2	..CCO.. C Cl
12	Trimethylene oxide	-19.2(g)	-18.8	-26.1	..CCCCO..
13	3,3-Dimethyloxetane	-35.4(g)	-34.4	-42.5	..CCCCO.. C
14	2,2-bis(chloromethyl) oxetane	-48.8(g)	-49.4	-62.8	..CCCCO.. CCI CCI

Some Oxygen-Containing Monomers and Polymers as Predicted by the New Bond-Energy Scheme^{a-d}

$\Delta H_f^\circ(\text{g})$ (pred.)	$\Delta H_f^\circ(\text{l})$ (pred.)	Heat of polymerization			Refs.
		$\Delta H_p^\circ(\text{gg})$ (pred.)	$\Delta H_p^\circ(\text{ll})$ (calc.)	$\Delta H_p^\circ(\text{xy})^c$	
(7)	(8)	(9)	(10)	(11)	(12)
-39.4	-41.7	-13.5	-10.7 -15.8(gl)	-15.9(gc)	9, 10, 34 59
-118.1	-125.0	-6.8	-6.4 -0.2(c''c)	-1.1(c''c)	9, 10, 59 72
-157.4	-164.9	-9.2	-8.1 +2.4(c''c)	-0.2(c''c)	10, 59, 72
-49.4	-52.3	-9.8	-6.3		9, 10, 89
-53.7	-57.1	-1.7	+1.9		2, 10
-59.0	-64.1	-9.5	-7.1	-8.5(ss) -5.9(sc)	2, 10, 88 89
-39.3	-42.6	-26.4	-23.6	-22.6(lc)	9, 10, 44
-69.4	-74.8	-19.3	-13.0		9, 10, 89
-55.5	-61.7	-25.4	-22.1		10, 89
-48.0	-52.0	-25.4	-22.7		9, 10, 89
-59.2	-64.5	-25.6	-22.3		6a, 10, 89
-44.2	-48.6	-25.4	-22.5	-19.2(ss)	9, 10, 44
-61.5	-67.0	-27.1	-24.5	-16.0(ss)	10, 44, 75
-70.4	-80.5	-21.0	-17.7	-20.2(lc)	10, 44, 75, 89

(continued)



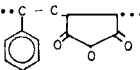
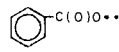
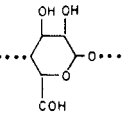
TABLE 5 (continued)

No.	Monomer	$\Delta H_f^\circ(x)$ (obsd.) ^f	$\Delta H_f^\circ(g)$ (pred.) ^g	$\Delta H_f^\circ(l)$ (calc.) ^h	Polymer structure (repeat unit)
(1)	(2)	(3)	(4)	(5)	(6)
15	Tetrahydrofuran	-44.0(g)	-44.1	-51.7	..CCCCO..
16	Tetrahydropyran	-53.4(g)	-54.0	-62.4	..CCCCCO..
17	1,3-Dioxolane	-72.1(g)	-72.6	-80.6	..CCOCO..
18	Oxepane	-57.5(g)	(-58.9)*	[-67.0]	..CCCCCO..
19	1,3-Dioxepane	-83.5(g)	(-88.5)*	[-93.3]	..CCCCOCO..
20	Acrolein		-16.8	-27.6	..CC.. C O
21	Acrylic acid	-80.5(g)	-80.5	-91.7	..CC.. CO O
22	Methyl acrylate		-76.0	-83.9	..CC.. CO OC
23	Methacrylic acid	-103.6(l)	-89.7	-101.8	..CC.. CO O
24	Methyl methacrylate	-92.7(l)	-85.1	-93.7	..CC.. CO OC
25	Methyl- α -chloroacrylate		-83.1	-97.0	..CC.. CO
26	Vinyl alcohol (hypothetical)		-30.0	-41.9	..CC.. O
27	Vinyl acetate		-78.6	-86.5	..CC.. O OCC
28	Isopropenyl acetate		-87.7	-96.3	..CC.. O OCC

$\Delta H_f^\circ(\text{g})$ (pred.)	$\Delta H_f^\circ(\text{l})$ (pred.)	Heat of polymerization			Refs.
		$\Delta H_p^\circ(\text{gg})$ (pred.)	$\Delta H_p^\circ(\text{ll})$ (calc.)	$\Delta H_p^\circ(\text{xy})^c$	
(7)	(8)	(9)	(10)	(11)	(12)
-49.1	-54.6	-5.0	-2.9	-1.8(lc)	9, 10, 59, 89
-54.0	-60.6	0.0	+1.8		2, 10
-78.6	-83.6	-6.0	-3.0	-3.5(lc)	10, 59, 89
-58.9	-66.7	-1.4	+0.3	+0.4(lc)	10, 59
-88.5	-96.4	-5.0	-3.1	-3.1(lc)	10, 59
-35.4	-42.6	-18.6	-15.0	-19.1(lc)	10, 44
-99.1	-107.4	-18.6	-15.7	-16.0(lc) -18.4(ss)	9, 10 44
-94.6	-102.1	-18.6	-18.2	-18.8(lc)	10, 44
(-105.5)*	(114.3)*	(-15.8)*	(-12.5)*	-15.8(ss) -10.1(lc)	9, 10, 44
(-100.9)*	(-108.5)*	(-15.8)*	(-14.8)*	-14.0(ss) -13.0(lc)	9, 10, 44
(-103.5)*	(-116.2)*	(-20.4)*	(-19.2)*		10
-49.4	-57.1	-19.4	-15.2		10, 89
-100.0	-107.1	-21.4	-20.6	-21.0(lc)	9, 10, 44
(-109.4)*	(-116.6)*	(-21.7)*	(-20.3)*		10

(continued)

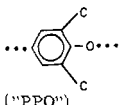
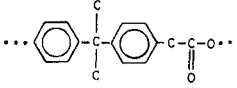
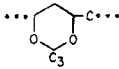

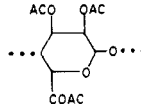
TABLE 5 (continued)

No.	Monomer	$\Delta H_f^{\circ}(x)$ (obsd.) ^f	$\Delta H_f^{\circ}(g)$ (pred.) ^g	$\Delta H_f^{\circ}(l)$ (calc.) ^h	Polymer structure (repeat unit)
(1)	(2)	(3)	(4)	(5)	(6)
29	Vinyl chloroformate		-71.7	-83.4	..CC.. O OCCl
30	Vinyl trifluoroacetate		-230.1	-240.4	..CC.. O OCCF ^{'''}
31	Vinyl methyl ether		-25.5	-31.0	..CC.. O C
32	Vinyl methyl ketone		-29.2	-37.7	..CC.. CO C
33	Vinylene carbonate	(-100.6)	-108.8	-119.5	...  ...
34	Maleic anhydride	-96.9(g)	[-96.9]	-108.4	...  ...
35	Styrene + maleic anhydride	+24.9(l)	-35.4 -96.9	+24.9 -108.4	...C - C... 
36	<i>o</i> -Hydroxyacetic acid - H ₂ O		-139.2 +57.8	-155.8 -68.3	..CC(O)O..
37	<i>o</i> -Hydroxyisobutyric acid - H ₂ O		-155.4 +57.8	-169.8 +68.8	C ..CC(O)O.. C
38	<i>m</i> -Acetoxybenzoic acid - H ₂ O		-114.4 +57.8	-136.3 +68.3	..  ..
39	Glucose - H ₂ O	-304.3(c'')	-263.3 +57.8	-295.9 +68.3	...  ...

$\Delta H_f^\circ(\text{g})$ (pred.)	$\Delta H_f^\circ(\text{l})$ (pred.)	Heat of polymerization		$\Delta H_p^\circ(\text{xy})^c$	Refs.
		$\Delta H_p^\circ(\text{gg})$ (pred.)	$\Delta H_p^\circ(\text{ll})$ (calc.)		
(7)	(8)	(9)	(10)	(11)	(12)
-93.1	-101.9	-21.4	-18.5		10, 89
-251.5	-258.8	-21.4	-18.4		10
-44.9	-48.9	-19.4	-17.9		10, 89
-47.8	-55.1	-18.6	-17.4	-17.7(1c)	10, 44
125.3	-130.9	-16.5	-11.4		55, 89, 63
-117.5	-126.1	-20.6	-17.7	-14(1s)	10, 44, 55
-100.9	-118.1	$\frac{1}{2}(-39.4)$	$\frac{1}{2}(-35.6)$	-19.7(ss)	9, 10, 44, 89
-86.4	-92.0	$(-5.0)^i$	$(-4.5)^i$		10, 89
-102.6	-108.7	$(-5.0)^i$	$(-7.2)^i$		10, 89
-61.6	-72.7	$(-5.0)^i$	$(-4.7)^i$		10, 89
-210.5	-228.8	$(-5.0)^j$	$(-1.2)^j$		10, 89

(continued)

TABLE 5 (continued)

No.	Monomer	$\Delta H_f^c(x)$ (obsd.) ^f	$\Delta H_f^c(g)$ (pred.) ^g	$\Delta H_f^c(l)$ (calc.) ^h	Polymer structure (repeat unit)
(1)	(2)	(3)	(4)	(5)	(6)
40	2,6-Dimethyl phenol + $\frac{1}{2}O_2 - H_2O$		-38.4 -57.8	-53.6 -68.3	 ("PPPO")
41	2,2-bis(4-Hydroxyphenyl)- propane + Phosgene - 2HCl		-56.6 -52.5 2(+22.0)	-82.2 -65.0 2(+25.9)	 ("Lexan")
42	Polyvinylene carbonate + H ₂ O - CO ₂		-125.3 -57.8 +94.1	-130.9 -68.3 +95.4	..CC... OO (Polyhydroxymethylene)
43	2(Polyvinyl alcohol) + Butyraldehyde - H ₂ O		2(-49.4) -49.5 +57.8	2(-57.1) -57.0 +68.3	 (Polyvinyl outyral)
44	Terephthalic acid + Ethylene glycol - 2H ₂ O		-166.2 -92.1 2(+57.8)	-188.5 -107.4 2(+68.3)	...OOC  COOC-C... (Polyethylene terephthalate)
45	Cellulose + 1 $\frac{1}{2}$ Acetic anhydride - 1 $\frac{1}{2}$ H ₂ O		-210.5 1 $\frac{1}{2}$ (-138.7) 1 $\frac{1}{2}$ (+57.8)	-228.8 1 $\frac{1}{2}$ (-149.2) 1 $\frac{1}{2}$ (-68.3)	 (Cellulose triacetate)
46	1,3-Dioxecane	-	[-87.6]*	[-93.4]*	..CCCCOCO..
47	1,3,6-Trioxecane	-	[-114.2]*	[-117.9]*	..CCOCCOCO..

^aValues in parentheses with asterisk are the basic bond energy contribution only, since strain energy

^bValues in square brackets are observed values.

^cValues in square brackets with asterisk are observed values derived from $\Delta H_p^c(g)$ of polymerization

^dPhase specification: (g) = gas, (l) = liquid, (c) = condensed solid of undefined crystallinity,

^eExperimental value: estimated entirely experimentally.

^fObserved value: essentially an experimental value, but may include a calculated enthalpy of

^gPredicted value: predicted entirely from correlation procedures.

^hCalculated value: essentially a predicted value, but may include experimental value of phase change.

ⁱHeat of polycondensation (diesterification).

^jHeat of polyether formation.

^kHeat of oxidative coupling.

^lHeat of polyesterification through phosgene.

^mHeat of hydrolysis of poly(vinylene carbonate) with plain water.

ⁿHeat of acetal condensation.

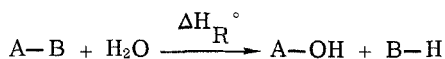
^oHeat of triple esterification through acid anhydride.

$\Delta H_f^\circ(\text{g})$ (pred.)	$\Delta H_f^\circ(\text{l})$ (pred.)	Heat of polymerization			Refs.
		$\Delta H_p^\circ(\text{gg})$ (pred.)	$\Delta H_p^\circ(\text{ll})$ (calc.)	$\Delta H_p^\circ(\text{xy})^c$	
(7)	(8)	(9)	(10)	(11)	(12)
-23.6	-34.1	(-43.0) ^k	(-48.8) ^k		9, 10, 89 91
-97.8	-116.8	(-32.8) ^l	(-21.4) ^l		9, 10, 89, 91
-89.0	-100.9	(0.0) ^m	(+2.9) ^m		10, 89
-104.8	-113.2	(-14.3) ⁿ	(-10.3) ⁿ		10, 89
-152.7	-169.9	(-10.0) ⁱ	(-10.6) ⁱ		10, 89
-410.2	-426.5	(-78.3) ^o	(-76.3) ^o		10, 89
-93.4	-102.4	-	-	-14.8(gc)	10, 59d
-117.9	-129.1	-	-	-14.9(gc)	10, 59d

of ring, resonance energy of special kind, or the 1-4 interaction in polymer is unpredictable.
equilibrium [59d].

(s) = solution, (c^{''}) = fully crystalline solid, (gg) = gas to gas, and (ll) = liquid to liquid, etc.
phase change.

theoretical interest. The bond-energy scheme is more versatile in this regard than the group-contribution method due to its more distinct and clear-cut energy terms for various bonds broken and formed in chemical reactions. From the $\Delta H_f^\circ(g)$ of some cyclic ketones in Table 4 (viz., compounds Nos. 18, 54, 70, etc.), the energy of keto-enol tautomerism and the energy of aromatization of conjugated systems may be readily worked out. The heat of formation and polymerization of "vinyl alcohol" (compound No. 26) and the polycondensation of glucose to cellulose (compound No. 39) by elimination of water molecule are also hypothetical cases. In Table 6 the enthalpies of gas-phase hydrolysis, viz., the general reaction



in respect of alkyl and acyl halides, anhydrides, esters, and ethers, are calculated using the appropriate bond-energy terms developed in this work.

TABLE 6. Heats of Gas Phase Hydrolysis of (A-B) in kcal/mole at 25°C^a

A	B					
	F	Cl	Br	I	R ₁ -COO	R ₂ -O
CH ₂ -	-0.8	+6.2	-8.6	+10.1		
CH-	-3.1	+5.2	+7.6	+9.0		
C-	-4.3	+5.5	+6.3	+7.2		
φ-	-2.2	+0.9	+1.3	+2.0		
C=C-	-4.7	-1.0	+0.4	+1.6		
R ₁ -CO-	-4.1	-11.4	-7.9	-6.8	-10.2	+5.0
R ₁ -	-	-	-	-	-	+5.0

^aA negative sign indicates that the enthalpy is in favor of hydrolysis and a positive sign that it favors H₂O elimination. For such hydrolysis/dehydration reactions, usually carried out in the solution phase, the above pattern changes radically [103] due to the heats of mixing, H-bonding, and dilution of the products of hydrolysis, especially the acids with water which is generally used as a medium.

Heats of polymerization range from 0 to 15 kcal/mole for polymerization through the carbonyl bond, from 10 to 24 kcal/mole (and up to 40 kcal/mole for fluorocarbon monomers) for vinyl polymerization, and from 0 to 24 kcal/mole for polymerization through ring opening depending upon the ring strain. It is possible to calculate the enthalpy of any specific polymerization reaction on the basis of the bond additivity scheme with a precision of ± 2 kcal/mole, except for polycyclic monomers which have been listed separately in the earlier part of this work [1c].

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Note Added in Proof. Recent accurate thermochemical data of J. O. Fenwick et al. [J. Chem. Thermodyn., **7**, 943 (1975)] calls for additional steric correction terms for the 1-3 interactions such as C-X-C for oxygen compounds. In the present paper the existing terms for hydrocarbons ($X = C$) taken from Part II of this series [1b] have been applied but are found to be inadequate. The new 1-3 interaction terms in oxygen compounds will be $C_0^3-O-C_3^3 = 2.1$ and $C_0^3-O-C_0^3 = 9.4$ kcal/mole, where the subscripts on carbon atoms indicate the number of hydrogen atoms.