Group Increments (in kcal/mol) for Fundamental Groupings*

Group	ΔH_f°	Group	ΔH_f°	Group	ΔH_f°
C–(H)$_3$(C)	–10.20	C–(O)(C$_d$)(H)$_2$	–6.5	C–(O)$_2$(C)$_2$	–18.6
C–(H)$_2$(C)$_2$	–4.93	C$_B$–(O)	–0.9	C–(O)$_2$(C)(H)	–16.3
C–(H)(C)$_3$	–1.90	O–(C)$_2$	–23.2	C–(O)$_2$(H)$_2$	–16.1
C–(C)$_4$	0.50	O–(C)(H)	–37.9	C–(N)(H)$_3$	–10.08
C$_d$–(H)$_2$	6.26	O–(C$_d$)$_2$	–33.0	C–(N)(C)(H)$_2$	–6.6
C$_d$–(H)(C)	8.59	O–(C$_d$)(C)	–30.5	C–(N)(C)$_2$(H)	–5.2
C$_d$–(C)$_2$	10.34	O–(C$_B$)$_2$	–21.1	C–(N)(C)$_3$	–3.2
C$_d$–(C$_d$)(H)	6.78	O–(C$_B$)(C)	–23.0	C$_B$–(N)	–0.5
C$_d$–(C$_d$)(C)	8.88	O–(C$_B$)(H)	–37.9	N–(C)(H)$_2$	4.8
C$_d$–(C$_B$)(H)	6.78	C–(CO)(C)$_3$	1.58	N–(C)$_2$(H)	15.4
C$_d$–(C$_B$)(C)	8.64	C–(CO)(C)$_2$(H)	–1.83	N–(C)$_3$	24.4
C$_d$–(C$_d$)$_2$	4.6	C–(CO)(C)(H)$_2$	–5.0	N–(C$_B$)(H)$_2$	4.8
C$_B$–(H)	3.30	C–(CO)(H)$_3$	–10.08	N–(C$_B$)(C)(H)	14.9
C$_B$–(C)	5.51	C$_B$–(CO)	9.7	N–(C$_B$)(C)$_2$	26.2
C$_B$–(C$_d$)	5.68	CO–(C)$_2$	–31.4	N–(C$_B$)$_2$(H)	16.3
C$_B$–(C$_B$)	4.96	CO–(C)(H)	–29.1	N$_I$–(H)	16.3
C–(C$_d$)(C)(H)$_2$	–4.76	CO–(H)$_2$	–26.0	N$_I$–(C)	21.3
C–(C$_d$)$_2$(H)$_2$	–4.29	CO–(C$_B$)$_2$	–25.8	N$_I$–(C$_B$)	16.7
C–(C$_d$)(C$_B$)(H)$_2$	–4.29	CO–(C$_B$)(C)	–30.9	CO–(N)(H)	–29.6
C–(C$_B$)(C)(H)$_2$	–4.86	CO–(C$_B$)(H)	–29.1	CO–(N)(C)	–32.8
C–(C$_d$)(C)$_2$(H)	–1.48	CO–(O)(C)	–35.1	N–(CO)(H)$_2$	–14.9
C–(C$_B$)(C)$_2$(H)	–0.98	CO–(O)(H)	–32.1	N–(CO)(C)(H)	–4.4
C–(C$_d$)(C)$_3$	1.68	CO–(O)(C$_d$)	–32.0	N–(CO)(C)$_2$	—
C–(C$_B$)(C)$_3$	2.81	CO–(O)(C$_B$)	–36.6	N–(CO)(C$_B$)(H)	0.4
C–(O)(C)$_3$	–6.6	CO–(C$_d$)(H)	–29.1	N–(CO)$_2$(H)	–18.5
C–(O)(C)$_2$(H)	–7.2	O–(CO)(C)	–43.1	N–(CO)$_2$(C)	–5.9
C–(O)(C)(H)$_2$	–8.1	O–(CO)(H)	–58.1	N–(CO)$_2$(C$_B$)	–0.5
C–(O)(H)$_3$	–10.08	C$_d$(CO)(C)	7.5		
C–(O)(C$_B$)(H)$_2$	–8.1	C$_d$–(CO)(H)	5.0		

Table 2.7
Group Increment Values for Free Radicals (kcal/mol)*

Radical	ΔH_f°	Radical	ΔH_f°
[•C–(C)(H)$_2$]	35.82	[C–(O•)(C)(H)$_2$]	6.1
[•C–(C)$_2$(H)]	37.45	[C–(O•)(C)$_2$(H)]	7.8
[•C–(C)$_3$]	38.00	[C–(O•)(C)$_3$]	8.6
[•C–(H$_2$)(C$_d$)]	23.2	[C–(CO$_2$•)(H)$_3$]	–47.5
[•C–(H)(C)(C$_d$)]	25.5	[C–(CO$_2$•)(H)$_2$(C)]	–41.9
[•C–(C)$_2$(C$_d$)]	24.8	[C–(CO$_2$•)(H)(C)$_2$]	–39.0
[•C–(C$_B$)(H)$_2$]	23.0	[•N–(H)(C)]	(55.3)
[•C–(C$_B$)(C)(H)]	24.7	[•N–(C)$_2$]	(58.4)
[•C–(C$_B$)(C)$_2$]	25.5	[C–(•N)(C)(H)$_2$]	–6.6
[C–(C•)(H)$_3$]	–10.08	[C–(•N)(C)$_2$(H)]	–5.2
[C–(C•)(C)(H)$_2$]	–4.95	[C–(•N)(C)$_3$]	(–3.2)
[C–(C•)(C)$_2$(H)]	–1.90	[•C–(H)$_2$(CN)]	(58.2)
[C–(C•)(C)$_3$]	1.50	[•C–(H)(C)(CN)]	(56.8)
[C$_d$–(C•)(H)]	8.59	[•C–(C)$_2$(CN)]	(56.1)
[C$_d$–(C•)(C)]	10.34	[•N–(H)(C$_B$)]	38.0
[C$_B$–C•]	5.51	[•N–(C)(C$_B$)]	42.7
[C–(•CO)(H)$_3$]	–5.4	[C$_B$–N•]	–0.5
[C–(•CO)(C)$_2$(H)]	2.6		
[C–(•CO)(C)(H)$_2$]	–0.3		

C$_d$ = double bond; C$_B$ = benzene carbon; N$_I$ = imine nitrogen. Values in parentheses are highly approximate.

*Data are from Benson, S. W. (1976). *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2d ed., John Wiley & Sons, New York.