detectable down to levels corresponding to yields of approximately 0.1%. Any peak whose area never represented more than 2% of the total area due to all product peaks was not investigated. Peak areas were determined using a Varian CDS 111L integrator. Yields were determined by comparisons of areas of absorption for each component relative to that of an alkane standard. For the reaction of **1** with dipropylmagnesium, undecane was the internal standard and the GC conditions were 2 min at 45 °C followed by an increase of 50 °C per min to 130 °C, which temperature then was maintained. Retention times (min) and response factors (for equal weights) were **1** (1.52, 1.38), **4** (1.97, 1.20), undecane (3.68, 1.00), and **2** (4.17, 1.08). For the reactions with **5**, it was assumed that the detector responded equally to equal weights of different compounds. For the reaction with dipropylmagnesium, pentadecane was the internal standard and the GC conditions were 2 min at 55 °C followed by an increase of 55 °C per min to 160 °C, which temperature then was maintained. Retention times (min) were **5** (2.20), **8** (2.79), **6** (4.25), and pentadecane (5.40). For the reaction with di-*tert*-butylmagnesium, hexadecane was the internal standard and the GC conditions were 45 °C for 3 min followed by an increase of 60 °C per min to 200 °C, which temperature then was maintained. Retention times (min) were **5** (2.80), **8** (3.81), **7** (5.91), and hexadecane (6.53).

Reaction of Ethylpotassium and 1. A sample of Na–K alloy prepared[37] by pushing together Na (0.15 g, 6.5 mmol) and K (0.78 g, 20 mmol) was added to cyclohexane (10 mL). To the stirred suspension was added dropwise over 15 minutes a solution of Et_2Hg (1.68 g, 6.5 mmol) in cyclohexane (3 mL), and the resulting mixture was stirred for 24 h. Excess alloy was removed by addition of mercury,[38] stirring for 2 h, and decanting the suspension of EtK from the solid. Decane (as a GC standard) and **1** (0.24 g, 2.1 mmol) were added to this suspension. The reaction mixture was stirred for 18 h and quenched with a saturated aqueous NH_4Cl solution. The organic layer was dried (Na_2SO_4). GC conditions were similar to those reported for reactions of **1** above; a response factor of 1.1 was assumed for **3**.

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Registry No. **1**, 565-80-0; **2**, 51200-81-8; **3**, 3970-59-0; **4**, 600-36-2; **5**, 815-24-7; **6**, 32579-69-4; **7**, 41902-42-5; **8**, 14609-79-1; EtK, 4522-40-1; Et_2Hg, 627-44-1; Pr_2Mg, 4907-44-2; *t*-Bu_2Mg, 14627-81-7; MeOK, 865-33-8; *t*-BuOK, 865-47-4; PhOK, 100-67-4; $(Me_2NCH_2)_2CHOK$, 126083-47-4; MeONa, 124-41-4; MeOLi, 865-34-9; *t*-BuOLi, 1907-33-1; Bu_4NBr, 1643-19-2; $BzlEt_3NCl$, 56-37-1; $PhCH_2OK$, 22379-62-0; 2,1,1-cryptand, 31250-06-3; 2,2,2-cryptand, 23978-09-8; propyl bromide, 106-94-5; *tert*-butyl chloride, 507-20-0.

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Estimation of Free Radical Group Enthalpy of Formation Values. Application to Estimation of Bond Dissociation Energies in Perfluoroalkylbenzenes

Wendell L. Dilling

Organic Chemicals and Polymers Laboratory, Central Research, The Dow Chemical Company, Midland, Michigan 48674

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A correlation has been observed between the differences in Benson's group enthalpies of formation for free radicals, {[$^{\bullet}$C-(X)(Y)(Z)] – [$^{\bullet}$C-(H)(Y)(Z)]}, and the related molecules, {[C-(H)(X)(Y)(Z)] – [C-$(H)_2$(Y)(Z)]}, where X = C, C_B, C_d, C_t, CN, CO, Br, Cl, F, I, N, NO_2, O, or Si, and Y and Z = H or the same X atoms or groups except Si. The least squares equation, [$^{\bullet}$C-(X)(Y)(Z)] (kcal mol^{-1}) = [$^{\bullet}$C-(H)(Y)(Z)] + (0.857 ± 0.031){[C-(H)(X)(Y)(Z)] – [C-$(H)_2$(Y)(Z)]} – (4.64 ± 0.62), $r^2 = 0.90$, $n = 89$, provides a way to estimate unknown radical group values when the other three group values in the equation are known. Numerous new radical group values were derived from experimental enthalpies of formation for use in this correlation. Analogous equations were also derived for the specific cases where X is only one of the atoms or groups indicated. Applications of these equations for estimating the benzylic bond dissociation energies for the perfluoroalkylbenzenes are reported; $D(PhCF_2\text{–}R_f)$ = 112, 78, and 70 kcal mol^{-1} for R_f = F, CF_3, and CF_2CF_3, respectively.

Introduction

Benson and co-workers have developed a useful method for predicting enthalpies of formation of molecules and free radicals from constituent group values.[1] The utility of this method for free radicals is limited because of the lack of many of the required group values, [$^{\bullet}$C-(X)(Y)(X)]. In the course of another research project where we needed to estimate the enthalpies of formation of several halogenated

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free radicals, the available compilations gave no group values for such radicals, e.g. [$^\bullet$C-(C_B)(F)$_2$].[1d] This paper describes a method to make such estimates and an application of the method to estimate the benzylic bond dissociation energies for the perfluoroalkylbenzenes, $PhCF_3$, $PhCF_2CF_3$, and $PhCF_2CF_2CF_3$.

Results and Discussion

To estimate a radical-centered group value, [$^\bullet$C-(X)(Y)(Z)], we reasoned that perhaps one could use an atom substitution principle to arrive at a useful relationship between (1) the difference in values of the group in question and of the corresponding radical-centered group with one of the substituent atoms or groups replaced by a hydrogen atom, [$^\bullet$C-(H)(Y)(Z)], and (2) the difference in values of the corresponding nonradical analogues where the radical centers were replaced by hydrogen atoms, [C-(H)(X)(Y)(Z)] and [C-(H)$_2$(Y)(Z)]. In other words, perhaps a relationship exists between the stabilizing effect of an atom or group on a radical and the stabilizing effect of that same atom or group on a neutral molecule. If a relationship does exist, then one could calculate [$^\bullet$C-(X)(Y)(Z)] if values for the other three groups were known. In general, many more group values are known for nonradicals than for radicals, and more values for simple radicals are known than for more complex radicals. Of course the relationship could be used two or more times to go from [$^\bullet$C-(X)(Y)(X)] to [$^\bullet$C-(H)(Y)(Z)] to [$^\bullet$C-(H)$_2$(Z)] to even [$^\bullet$C-(H)$_3$].

To test whether a relationship does exist between [$^\bullet$C-(X)(Y)(Z)] - [$^\bullet$C-(H)(Y)(Z)] and [C-(H)(X)(Y)(Z)] - [C-(H)$_2$(Y)(Z)], we collected data where all four values were available. Several sets, where X = C, C_B, C_d, and CN, were taken from Benson's compilation.[1d] A few sets, where X = CN, Br, Cl, F, I, and NO_2, were available from the radical or molecular values, e.g. [$^\bullet$C-(H)(F)$_2$] = $\Delta H_f°(^\bullet CHF_2)$, [C-(H)$_2(F)_2$] = $\Delta H_f°(CH_2F_2)$. Other values (Table I) for radical groups in sets where at least one of X, Y, or Z is a multivalent atom or group, C, C_B, C_d, C_t, CO, N, O, or Si, were derived from reported enthalpies of formation of various free radicals, $^\bullet$CX′Y′Z′, and known group values, from eq 1, where [X-(C$^\bullet$)...] = [X-(C)...], etc.[1c,d,7] The last three terms of eq 1 appear only if the X, Y, or Z is multivalent. Most of the reported enthalpies of formation used here are from experimental data; a few are from theoretical calculations or are estimates. No sets in which all four group values had been reported or were derivable from experimental data that were known to us at the time this work was completed have been omitted from the correlation. The data for 89 sets are given in Table II and are plotted in Figure 1.

$$[^\bullet\text{C-(X)(Y)(Z)}] = \Delta H_f°(^\bullet\text{CX}'\text{Y}'\text{Z}') - \{[\text{X-(C}^\bullet)...] + ...\} - \{[\text{Y-(C}^\bullet)...] + ...\} - \{[\text{Z-(C}^\bullet)...] + ...\} \quad (1)$$

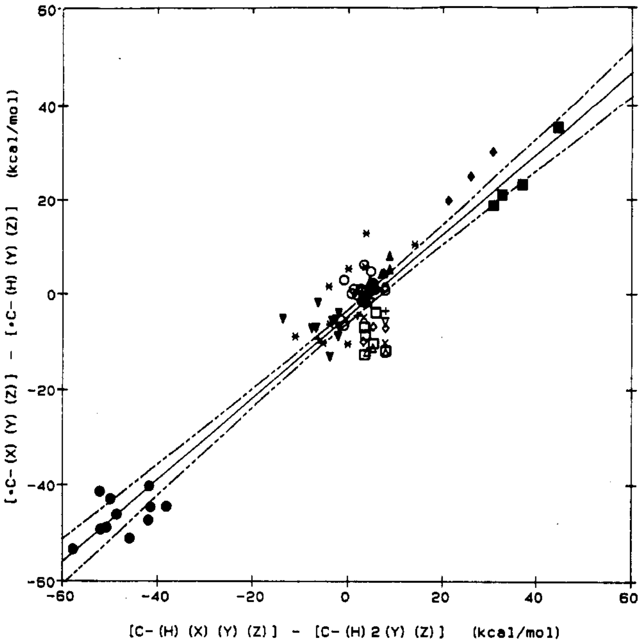

Figure 1. Correlation of differences in group enthalpies of formation for radicals and molecules. Symbols for X atoms or groups: C (○), C_B (△), C_d (□), C_t (◇), CN (■), CO (▽), Br (▲), Cl (▼), F (●), I (◆), N (×), NO_2 (*), O (+), Si (0). Equation of least squares line (std dev given): [$^\bullet$C-(X)(Y)(Z)] - [$^\bullet$C-(H)(Y)(Z)] = (0.857 ± 0.031){[C-(H)(X)(Y)(Z)] - [C-(H)$_2$(Y)(Z)]} - (4.64 ± 0.62), $r^2 = 0.90$, $n = 89$, 95% confidence curves shown.

For internal consistency we have retained most group and molecular values given in Benson's compilation[1d] even though more recent studies indicate that perhaps some revisions should be made.[36] Although desirable, a complete revision of the group values given by Benson[1d] would require considerable effort. Some revised molecular values

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Table I. Derivation of Radical Group Enthalpies of Formation from Known Radical Enthalpies of Formation[a]

X	Y	Z	X′	Y′	Z′	ΔH_f° ($^\bullet$CX′Y′Z′)	[X–(C$^\bullet$)...] + ...	[Y–(C$^\bullet$)...] + ...	[Z–(C$^\bullet$)...] + ...	[$^\bullet$C–(X)(Y)(Z)]
C	H	Br	CH_3	H	Br	28.45[b]	-10.08[c]			38.53
C	H	Cl	CH_3	H	Cl	18.3[d]	-10.08[c]			28.4
			CH_2Cl	H	Cl	14.4[e]	-16.5[c]			30.9
			$CHCl_2$	H	Cl	8.70[e]	-18.9[c]			27.6
										28.97 ± 0.99[f]
C	H	F	CH_3	H	F	-18.9[g]	-10.08[c]			-8.8
C	H	N	CH_3	H	NH_2	26[h]	-10.08[c]		4.8[c]	31
C	H	NO_2	CH_3	H	NO_2	14.8[e]	-10.08[c]			24.9
			CH_2CH_3	H	NO_2	12.3[e]	-4.95 - 10.08[i]			27.3
			$CH_2CH_2CH_3$	H	NO_2	5.09[e]	2(-4.95) - 10.08[i]			25.07
										25.76 ± 0.79[f]
C	C	C_t	CH_3	CH_3	C≡CH	61.5[j]	-10.08[c]	-10.08[c]	27.55 + 26.93[c]	27.2
			CH_3	CH_3	C≡CCH_3	53.0[k]	-10.08[c]	-10.08[c]	2(27.55) - 10.08[i]	28.1
										27.66 ± 0.48[l]
C	C	N	CH_3	CH_3	NH_2	17[h]	-10.08[c]	-10.08[c]	4.8[c]	32
C	C	NO_2	CH_3	CH_3	NO_2	8.51[e]	-10.08[c]	-10.08[c]		28.67
C	C	O	CH_3	CH_3	OH	-26.6[j]	-10.08[c]	-10.08[c]	-37.9[c]	31.5
C	C_B	CN	CH_3	C_6H_5	CN	54.4[j]	-10.08[c]	5.51 + 5(3.30)[c]		42.5
C	C_t	H	CH_3	C≡CH	H	72.4[m]	-10.08[c]	27.55 + 26.93[c]		28.0
			CH_3	C≡CCH_3	H	65.2[k]	-10.08[c]	2(27.55) - 10.08[i]		30.3
										29.1 ± 1.1[l]
C	CO	H	CH_3	$COCH_3$	H	-17.4[n]	-10.08[c]	-31.4 - 10.08[c]		34.1
C	Cl	Cl	CH_3	Cl	Cl	12.6[e]	-10.08[c]			22.7
			CH_2Cl	Cl	Cl	7.41[e]	-16.5[c]			23.9
			$CHCl_2$	Cl	Cl	5.7[o]	-18.9[c]			24.6
			CCl_3	Cl	Cl	7.6[p]	-20.7[c]			28.3
										23.73 ± 0.56[q]
C	F	F	CH_3	F	F	-70.7[o]	-10.08[c]			-60.6
			$CClF_2$	F	F	-164[j]	-106.3[c]			-58
			CF_3	F	F	-216[o]	-161[c]			-55
										-57.7 ± 1.7[f]
C	F	NO_2	$CF(NO_2)_2$	F	NO_2	-50.0[e]	-46.9[r]			-3.1
C	NO_2	NO_2	CH_3	NO_2	NO_2	21.7[e]	-10.08[c]			31.8
			CH_2CH_3	NO_2	NO_2	15.7[e]	-4.95 - 10.08[i]			30.7
			$CH_2CH_2CH_3$	NO_2	NO_2	10.6[e]	2(-4.95) - 10.08[i]			30.6
			$CF(NO_2)_2$	NO_2	NO_2	-7.89[e]	-46.9[r]			39.0
										31.03 ± 0.38[q]
C_d	H	Cl	CH=CH_2	H	Cl	36.4[s]	8.59 + 6.26[c]			21.5
C_d	H	O	CH=CH_2	H	OH	0.0[j]	8.59 + 6.26[c]		-37.9[c]	23.1
C_d	C_d	H	CH=CH_2	CH=CH_2	H	49[k]	8.59 + 6.26[c]	8.59 + 6.26[c]		19
C_t	H	H	C≡CH	H	H	82.1[j]	27.55 + 26.93[c]			27.6
			C≡CCH_3	H	H	73.6[j]	2(27.55) - 10.08[i]			28.6
										28.10 ± 0.48[l]
CO	H	H	CHO	H	H	0.2[t]	-29.1[c]			29.3
			$COCH_3$	H	H	-12[t]	-31.4 - 10.08[c]			29[u]
										29.39 ± 0.09[l]
N	H	H	NH_2	H	H	33.2[v]	4.8[c]			28.4
			$NHCH_3$	H	H	30[h]	15.4 - 10.08[c]			25
			$N(CH_3)_2$	H	H	26.8[v]	24.4 - 2(10.08)[c]			22.5
										25.2 ± 1.1[f]
O	H	H	OH	H	H	-6.0[w]	-37.9[c]			31.9
			OCH_3	H	H	-2.0[x]	-23.2 - 10.08[c]			31.3
			$OCOC_6H_5$	H	H	-16.7[k]	-43.1 - 36.6 + 3.7 + 5(3.30)[c]			42.8
										31.58 ± 0.32[y]
O	H	O	OCH_3	H	OCH_3	-44.2[z]	-23.2 - 10.08[c]		-23.2 - 10.08[c]	22.4
Si	H	H	$Si(CH_3)_3$	H	H	-8.3[k]	-14.6 - 3(10.08)[a′]			36.5

[a] Enthalpies in kilocalories per mole, most at 298 K, a few at 300 K. [b] Mean of values given in refs 2 and 3. [c] Value from ref 1d. [d] Mean of values given in refs 3–5. [e] Value from ref 4. [f] Mean and standard deviation of three preceding entries. [g] Mean of values given in refs 4 and 5. [h] Value from ref 6. [i] See refs 1b,d and 7. [j] Value from ref 8. [k] Value from ref 9. [l] Mean and standard deviation of two preceding entries. [m] Value from ref 10. [n] Mean of values given in refs 8 and 11. [o] Mean of values given in refs 4 and 8. [p] Mean of values given in refs 4 and 12. [q] Mean and standard deviation of first three of four preceding entries. [r] Value from ref 13. [s] Calculated from $\Delta H_f^\circ(^\bullet CHClCH{=}CH_2) = D(H{-}CHClCH{=}CH_2) - \Delta H_f^\circ(H^\bullet) + \Delta H_f^\circ(CH_2{=}CHCH_2Cl)$, $D(H{-}CHClCH{=}CH_2) = 88.6$ kcal mol^{-1},[14] $\Delta H_f^\circ(H^\bullet) = 52.077$ kcal mol^{-1},[8] $\Delta H_f^\circ(CH_2{=}CHCH_2Cl) = -0.15$ kcal mol^{-1}.[15] [t] Value from ref 16. [u] If $\Delta H_f^\circ(^\bullet CH_2COCH_3) = -6.0$ kcal mol^{-1} [1d] is used, [$^\bullet$C-(CO)(H)$_2$] = 35.5 kcal mol^{-1}. [v] Mean of values given in refs 6 and 17. [w] Mean of values given in refs 8 and 18. [x] Mean of values given in refs 8 and 19. [y] Mean and standard deviation of first two of three preceding entries. [z] Value from ref 19. [a′] [Si-(C)$_4$] = ΔH_f°[Si(CH$_3$)$_4$] - 4[C-(H)$_3$(Si)], ΔH_f°[Si(CH$_3$)$_4$] = -54.9 kcal mol^{-1} (mean of values given in refs 20 and 21), [C–(H$_3$)(Si)] = -10.08 kcal mol^{-1} (see refs 1b,d, 7, and 22).

were used, e.g. ΔH_f°[Si(CH$_3$)$_4$], where more recent data indicate that the original values[1d] were in significant error. We have omitted error limits in the data cited because error limits in the original group values are not available.[1d] For the simpler, more thoroughly studied, groups the error limits are usually 1–2 kcal mol^{-1}; error limits for other groups may be significantly larger.

Within the limits of the scatter of the data in Figure 1 one can estimate the group enthalpy of formation for a new group, [$^\bullet$C-(X)(Y)(Z)], if the values of [$^\bullet$C-(H)(Y)(Z)], [C-(H)(X)(Y)(Z)], and [C-(H)$_2$(Y)(Z)] are known. Part of the scatter may be caused by errors in the experimental values on which the group values are based. For example, an older value for ΔH_f°($^\bullet$CHBr$_2$)[9] caused the data point for [$^\bullet$C-(H)(Br)$_2$] - [$^\bullet$C-(H)$_2$(Br)] to be significantly further off the correlation line than the more recent value actually used in the correlation. This correlation may even serve as a guide to group values that should be reevaluated.

Table II. Group Enthalpies of Formation for Radicals and Molecules[a]

X	Y	Z	[•C-(X)-(Y)(Z)]	[•C-(H)-(Y)(Z)]	[C-(H)-(X)(Y)-(Z)]	[C-(H)$_2$-(Y)(Z)]
C	H	H	35.82^{b}	35.1^{c}	-10.08^{d}	-17.9^{b}
C	H	Br	38.53^{e}	40.3^{f}	-5.4^{b}	-9.1^{b}
C	H	Cl	29.0^{e}	28.4^{f}	-16.5^{b}	-19.6^{b}
C	H	F	-8.8^{e}	-9.4^{g}	-51.5^{b}	-56^{b}
C	H	N	31^{e}	25^{e}	-6.6^{b}	-10.08^{b}
C	H	NO_2	25.8^{e}	24.7^{h}	-15.1^{b}	-17.86^{i}
C	H	O	31.4^{b}	31.6^{e}	-8.1^{b}	-10.08^{b}
C	C	H	37.45^{b}	35.82^{b}	-4.95^{d}	-10.08^{d}
C	C	C	38.00^{b}	37.45^{b}	-1.90^{b}	-4.95^{d}
C	C	C_B	25.5^{b}	24.7^{b}	-0.98^{b}	-4.86^{b}
C	C	C_d	24.8^{b}	25.5^{b}	-1.48^{b}	-4.76^{b}
C	C	C_t	27.7^{e}	29^{e}	-1.72^{b}	-4.73^{b}
C	C	CN	56.1^{b}	56.8^{b}	25.8^{b}	22.5^{b}
C	C	N	32^{e}	31^{e}	-5.2^{b}	-6.6^{b}
C	C	NO_2	28.67^{e}	25.8^{e}	-15.8^{b}	-15.1^{b}
C	C	O	31.5^{e}	31.4^{b}	-7.2^{b}	-8.1^{b}
C	C_B	H	24.7^{b}	23.0^{b}	-4.86^{b}	-10.08^{d}
C	C_d	H	25.5^{b}	23.2^{b}	-4.76^{b}	-10.08^{d}
C	C_t	H	29.1^{e}	28.1^{e}	-4.73^{b}	-10.08^{d}
C	CN	H	56.8^{b}	58.2^{b}	22.5^{b}	19^{j}
C	CO	H	34.1^{e}	29^{e}	-5.2^{b}	-10.08^{b}
C	Cl	Cl	23.7^{e}	22.9^{f}	-18.9^{b}	-22.8^{b}
C	F	F	-58^{e}	-58.7^{g}	-102.3^{b}	-108^{k}
C	NO_2	NO_2	31.0^{e}	37.5^{l}	-14.9^{b}	-14.1^{m}
C_B	H	H	23.0^{b}	35.1^{c}	-10.08^{d}	-17.9^{b}
C_B	C	H	24.7^{b}	35.82^{b}	-4.86^{b}	-10.08^{d}
C_B	C	C	25.5^{b}	37.45^{b}	-0.98^{b}	-4.95^{d}
C_d	H	H	23.2^{b}	35.1^{c}	-10.08^{d}	-17.9^{b}
C_d	H	Cl	21.5^{e}	28.4^{f}	-16.2^{n}	-19.6^{b}
C_d	H	O	23.1^{e}	31.6^{e}	-6.5^{b}	-10.08^{b}
C_d	C	H	25.5^{b}	35.82^{b}	-4.76^{b}	-10.08^{d}
C_d	C	C	24.8^{b}	37.45^{b}	-1.48^{b}	-4.95^{d}
C_d	C_d	H	19^{e}	23.2^{b}	-4.29^{b}	-10.08^{d}
C_t	H	H	28.1^{e}	35.1^{c}	-10.08^{d}	-17.9^{b}
C_t	C	H	29.1^{e}	35.82^{b}	-4.73^{b}	-10.08^{d}
C_t	C	C	27.7^{e}	27.45^{b}	-1.72^{b}	-4.95^{d}
CN	H	H	58.2^{b}	35.1^{c}	19^{j}	-17.9^{b}
CN	C	H	56.8^{b}	35.82^{b}	22.5^{b}	-10.08^{d}
CN	C	C	56.1^{b}	37.45^{b}	25.8^{b}	-4.95^{d}
CN	CN	H	93.67^{o}	58.2^{b}	63.5^{p}	19^{j}
CO	H	H	29.4^{e}	35.1^{c}	-10.08^{d}	-17.9^{b}
CO	C	H	34.1^{e}	35.82^{b}	-5.2^{b}	-10.08^{d}
Br	H	H	40.3^{f}	35.1^{c}	-9.1^{b}	-17.9^{b}
Br	H	Br	44.7^{f}	40.3^{f}	-1.4^{q}	-9.1^{b}
Br	C	H	38.53^{e}	35.82^{b}	-5.4^{b}	-10.08^{d}
Br	Br	Br	49.0^{q}	44.7^{f}	5.7^{r}	-1.4^{q}
Br	Cl	Cl	31^{s}	22.9^{f}	-14.0^{t}	-22.8^{k}
Cl	H	H	28.4^{f}	35.1^{c}	-19.6^{b}	-17.9^{b}
Cl	H	Cl	22.9^{f}	28.4^{f}	-22.8^{k}	-19.6^{b}
Cl	H	F	-14.5^{u}	-9.4^{g}	-69.5^{t}	-56^{b}
Cl	C	H	29.0^{e}	35.82^{b}	-16.5^{b}	-10.08^{d}
Cl	C	Cl	23.7^{e}	29.0^{e}	-18.9^{b}	-16.5^{b}
Cl	C_d	H	21.5^{e}	23.2^{b}	-16.2^{n}	-10.08^{d}
Cl	Br	Br	31.6^{v}	44.7^{f}	-5.0^{t}	-1.4^{q}
Cl	Cl	Cl	19.0^{w}	22.9^{f}	-24.6^{b}	-22.8^{k}
Cl	Cl	F	-23.2^{x}	-14.5^{u}	-71.4^{t}	-69.5^{t}
Cl	F	F	-65.6^{g}	-58.7^{g}	-115.4^{m}	-108^{k}
F	H	H	-9.4^{g}	35.1^{c}	-56^{b}	-17.9^{b}
F	H	Cl	-14.5^{u}	28.4^{f}	-69.5^{t}	-19.6^{b}
F	H	F	-58.7^{g}	-9.4^{g}	-108^{k}	-56^{b}
F	H	NO_2	-15.6^{y}	24.7^{h}	-59.63^{z}	-17.86^{i}
F	C	H	-8.8^{e}	35.82^{b}	-51.5^{b}	-10.08^{d}
F	C	F	-58^{e}	-8.8^{e}	-102.3^{b}	-51.5^{b}
F	Cl	Cl	-23.2^{x}	22.9^{f}	-71.4^{t}	-22.8^{k}
F	Cl	F	-65.6^{g}	-14.5^{u}	-115.4^{m}	-69.5^{t}
F	F	F	-112.0^{w}	-58.7^{g}	-165.7^{b}	-108^{k}
F	F	NO_2	-57.0^{h}	-15.6^{y}	-111.82^{z}	-59.63^{z}
F	NO_2	NO_2	$-9.9^{a'}$	37.5^{l}	-56.00^{m}	-14.1^{m}
I	H	H	54.9^{q}	35.1^{c}	3.3^{b}	-17.9^{b}
I	H	I	79.8^{w}	54.9^{q}	29.2^{b}	3.3^{b}
I	I	I	$110^{b'}$	79.8^{w}	$59.8^{c'}$	29.2^{b}
N	H	H	25^{e}	35.1^{c}	-10.08^{b}	-17.9^{b}
N	C	H	31^{e}	35.82^{b}	-6.6^{b}	-10.08^{d}
N	C	C	32^{e}	37.45^{b}	-5.2^{b}	-4.95^{d}
NO_2	H	H	24.7^{h}	35.1^{c}	-17.86^{i}	-17.9^{b}
NO_2	H	F	-15.6^{y}	-9.4^{g}	-59.63^{z}	-56^{b}
NO_2	H	NO_2	37.5^{l}	24.7^{h}	-14.1^{m}	-17.86^{i}
NO_2	C	H	25.8^{e}	35.82^{b}	-15.1^{b}	-10.08^{d}
NO_2	C	C	28.67^{e}	37.45^{b}	-15.8^{b}	-4.95^{d}
NO_2	C	NO_2	31.0^{e}	25.8^{e}	-14.9^{b}	-15.1^{b}
NO_2	F	F	-57.0^{h}	-58.7^{g}	-111.82^{z}	-108^{k}
NO_2	F	NO_2	$-9.9^{a'}$	-15.6^{y}	-56.00^{m}	-59.63^{z}
NO_2	NO_2	NO_2	47.90^{h}	37.5^{l}	-0.05^{m}	-14.1^{m}
O	H	H	31.6^{e}	35.1^{c}	-10.08^{d}	-17.9^{b}
O	H	O	22.4^{e}	31.6^{e}	-16.1^{b}	-10.08^{d}
O	C	H	31.4^{b}	35.82^{b}	-8.1^{b}	-10.08^{d}
O	C	C	31.5^{e}	37.45^{b}	-7.2^{b}	-4.95^{d}
O	C_d	H	23.1^{e}	23.2^{b}	-6.5^{b}	-10.08^{d}
Si	H	H	36.5^{e}	35.1^{c}	$-10.08^{d'}$	-17.9^{b}

[a] Group values in kilocalories per mole, most at 298 K, a few at 300 K. [b] Value from ref 1d. [c] Value from refs 8 and 23. [d] See refs 1b,d and 7. [e] This work. [f] Mean of values given in refs 3 and 24. [g] Mean of values given in refs 4 and 8. [h] Value from ref 4. [i] Value from refs 15 and 25. [j] Value from ref 23. [k] Value from refs 1d and 15. [l] Value from ref 26. [m] Value from ref 25. [n] Value from ref 27. [o] Value from ref 28; theoretical calculation. [p] Value from refs 28 and 29. [q] Value from ref 3. [r] Value from ref 30 cited in ref 3. [s] Calculated from $[^{\bullet}C{-}(Br)(Cl)_2] = D(CBrCl_2{-}Cl) - \Delta H_f°(Cl^{\bullet}) + \Delta H_f°(CBrCl_3)$, $D(CBrCl_2{-}Cl) = 70$ kcal mol^{-1},[31] $\Delta H_f°(Cl^{\bullet}) = 29.031$ kcal mol^{-1},[8] $\Delta H_f°(CBrCl_3) = -9.99$ kcal mol^{-1}.[25] [t] Value from ref 15. [u] Value from ref 24. [v] Calculated from $[^{\bullet}C{-}(Br)_2(Cl)] = D(CBr_2Cl{-}Br) - \Delta H_f°(Br^{\bullet}) + \Delta H_f°(CBr_3Cl)$, $D(CBr_2Cl{-}Br) = 55.5$ kcal mol^{-1},[31] $\Delta H_f°(Br^{\bullet}) = 26.86$ kcal mol^{-1},[8] $\Delta H_f°(CBr_3Cl) = 3.0$ kcal mol^{-1}.[15] [w] Value from ref 8. [x] Mean of values given in refs 4 and 24. [y] Value from refs 4 and 26. [z] Value from ref 32; theoretical calculation. [a'] Value from refs 26 and 33. [b'] Estimated value given in ref 34. [c'] Estimated value given in ref 35. [d'] Assigned value, $[C{-}(H)_3(Si)] = [C{-}(C)(H)_3]$.[1d]

Because the data for the sets where the same atom or group (X) has replaced a hydrogen atom tend to cluster (Figure 1), we have also treated these sets separately and calculated least-squares correlation lines for each (Table III). In general, the data points for those X atoms or groups that are part of radical stabilizing groups, especially C_B, C_d, and C_t, appear below the correlation line in Figure 1 as expected because of the lower enthalpy of [•C-(X)-(Y)(Z)] relative to [•C-(H)(Y)(Z)] compared to [C-(H)-(X)(Y)(Z)] relative to [C-(H)$_2$(Y)(Z)] for these atoms. Correlations for the combined saturated X atoms ($r^2 = 0.96$) and the combined unsaturated X atoms or groups ($r^2 = 0.95$), with NO_2 omitted because of excessive scatter ($r^2 = 0.66$ with NO_2 included), are given in Table III. For estimating new group values in this paper we have used the correlation equations for the specific X atoms or groups given in Table III because those should give more accurate values, if large extrapolations are not required, than using the general equations given in Figure 1 and the last three lines of Table III. If one needed to estimate a group value for which no correlation equation exists for a specific X atom or group, then either the overall correlation equation (Figure 1) or the equations for saturated or for unsaturated X atoms or groups could be used. Use of the overall correlation equation could potentially lead to larger errors, as much as 10 kcal mol^{-1} or so, in the estimated group values, but at least a rough estimate could be made.

As an example of the utility of the above correlations we estimated the benzylic bond dissociation energies of the perfluoroalkylbenzenes, $D(PhCF_2{-}R_f)$, where $R_f = F$, CF_3, and CF_2CF_3. All higher homologues have the same calculated benzylic bond dissociation energy as that of perfluoropropylbenzene, $R_f = CF_2CF_3$. The bond dissociation energy, defined by eq 2, can be estimated from the gen-

Table III. Least-Squares Correlations of Group Enthalpies of Formation for Radicals and Molecules for Single Atom or Group Replacement Types, $[{}^{\bullet}\text{C-(X)(Y)(Z)}] - [{}^{\bullet}\text{C-(H)(Y)(Z)}] = \text{Slope}\{[\text{C-(H)(X)(Y)(Z)}] - [\text{C-(H)}_2\text{(Y)(Z)}]\} + \text{Intercept}$

X	slope[a]	intercept[a,b]	*n*	max. dev[b]
C	0.42 ± 0.24	−0.84 ± 0.94	24	5.5
C_B	−0.09 ± 0.25	−11.2 ± 1.5	3	0.6
C_d	−0.20 ± 0.93	−8.1 ± 4.8	6	5.3
C_t	0.59 ± 0.45	−11.0 ± 2.6	3	1.2
CN	1.20 ± 0.18	−18.9 ± 6.5	4	2.3
CO	−1.36	4.9	2	
Br	0.94 ± 0.39	−2.1 ± 3.0	5	1.8
Cl	−0.16 ± 0.28	−7.1 ± 1.7	10	6.5
F	0.31 ± 0.20	−31.8 ± 9.7	11	6.5
I	1.11	−3.7	3[c]	
N	−0.62 ± 0.40	−4.2 ± 2.0	3	1.9
NO_2	0.96 ± 0.33	0.2 ± 2.2	9	10.7
O	0.49 ± 0.22	−5.2 ± 1.1	5	3.3
saturated[d]	0.908 ± 0.025	−3.01 ± 0.54	62	14.0
unsaturated[e]	1.068 ± 0.063	−14.3 ± 1.1	18	7.4
combination	0.857 ± 0.031	−4.64 ± 0.62	89	14.2

[a] Standard deviation given. [b] Kilocalories per mole. [c] One of the three values is an estimate.[34] [d] C, Br, Cl, F, I, N, O, Si. [e] C_B, C_d, C_t, CN, CO (NO_2 omitted).

Table IV. Estimated Benzylic Bond Dissociation Energies of Perfluoroalkylbenzenes ($PhCF_2R_f$) and Related Group Enthalpy of Formation Values

R_f	$[{}^{\bullet}\text{X-(Y)...}]$, kcal mol^{-1}	$[\text{C-(C}_B\text{)(F)}_2\text{-(X)}]$, kcal mol^{-1}	$[\text{X-(C)(Y)...}]$, kcal mol^{-1}	*D*-($PhCF_2$–R_f), kcal mol^{-1}
F	$[F^{\bullet}]$, 18.92[a]	$[\text{C-(C}_B\text{)(F)}_3]$, −162.7[b]		112
CF_3	$[{}^{\bullet}\text{C-(F)}_3]$, −112.0[a]	$[\text{C-(C)(C}_B\text{)-(F)}_2]$, −98[c]	$[\text{C-(C)(F)}_3]$, −161[b]	78
CF_2CF_3	$[{}^{\bullet}\text{C-(C)-(F)}_2]$, −58[d]	$[\text{C-(C)(C}_B\text{)-(F)}_2]$, −98[c]	$[\text{C-(C)}_2\text{(F)}_2]$, −99[b]	70

[a] Value from ref 8. [b] Value from ref 1d. [c] This work. [d] Value from Table I.

Table V. Comparison of Group Enthalpy of Formation Values of $[\text{C-(C)(X)(Y)(Z)}]$, $[\text{C-(C}_B\text{)(X)(Y)(Z)}]$, and $[\text{C-(C}_d\text{)(X)(Y)(Z)}]$[a]

X	Y	Z	$[\text{C-(C)(X)(Y)(Z)}]$	$[\text{C-(C}_B\text{)-(X)(Y)-(Z)}]$	$[\text{C-(C}_d\text{)-(X)(Y)(Z)}]$
C	H	H	−4.95	−4.86	−4.76
C	C	H	−1.90	−0.98	−1.48
C	C	C	0.50	2.81	1.68
C_d	H	H	−4.76	−4.29	−4.29
CO	H	H	−5.2	−5.4	−3.8
Br	H	H	−5.4	−5.1	
F	F	F	−161	−162.7	
I	H	H	8.0	8.4	
O	H	H	−8.1	−8.1	−6.5
S	H	H	−5.65	−4.73	−6.45
SO_2	H	H	−7.68	−5.54	−7.14

[a] Group values in kilocalories per mole from ref 1d.

Table VI. Estimated and Experimental Benzylic Bond Dissociation Energies of Alkylbenzenes ($PhCH_2R$)[a]

R	*D*($PhCH_2$–R)	$\Delta H_{25^\circ C}^{\ddagger}$ [b]
H	85.2	85.2,[c] 87.7[d]
CH_3	73.0	71.3[e], 72.1[f], 72.4[d]
CH_2CH_3	68.6	68.0,[d] 69.0[g]
$CH_2CH_2CH_3$	68.6[h]	66.5[d]

[a] Values in kilocalories per mole. [b] Calculated from $\Delta H_{25^\circ C}^{\ddagger} = E_a - 0.59$ and experimental E_a. [c] Value from ref 39. [d] Value from ref 40. [e] Value from ref 41. [f] Value from ref 42. [g] Value from ref 43. [h] This and all higher homologues have same values as for $PhCH_2CH_2CH_3$.

eralized group values in eq 3; all group values not involving the bond being broken cancel. The specific groups and their reported or derived values are shown in Table IV.

$$D(\text{PhCF}_2\text{–R}_f) = \Delta H_f^\circ(\text{PhCF}_2^{\bullet}) + \Delta H_f^\circ(\text{R}_f^{\bullet}) - \Delta H_f^\circ(\text{PhCF}_2\text{R}_f) \quad (2)$$

$$D(\text{PhCF}_2\text{–R}_f) = [{}^{\bullet}\text{C-(C}_B\text{)(F)}_2] + [{}^{\bullet}\text{X-(Y)...}] - [\text{C-(C}_B\text{)(F)}_2\text{(X)}] - [\text{X-(C)(Y)...}] \quad (3)$$

The group value, $[{}^{\bullet}\text{C-(C}_B\text{)(F)}_2]$, was estimated by two procedures, using the two equations in Table III where X = C_B and where X = F. In the former case, two of the required group values, $[{}^{\bullet}\text{C-(H)(F)}_2]$ and $[\text{C-(H)}_2\text{(F)}_2]$, are given in Table II. The third required value, $[\text{C-(C}_B\text{)(H)(F)}_2]$, was estimated from eq 4, which was derived from

$$[\text{C-(C}_B\text{)(X)(Y)(Z)}] - [\text{C-(C)(X)(Y)(Z)}] = 0.5 \quad (4)$$

the data in Table V; the means and standard deviations of $[\text{C-(C}_B\text{)(X)(Y)(Z)}] - [\text{C-(C)(X)(Y)(Z)}]$ and $[\text{C-(C}_B\text{)(X)(Y)(Z)}] - [\text{C-(C}_d\text{)(X)(Y)(Z)}]$ were 0.51 ± 0.33 and 0.21 ± 0.46 kcal mol^{-1}, respectively. From the known value of $[\text{C-(C)(H)(F)}_2]$ (Table II), $[\text{C-(C}_B\text{)(H)(F)}_2]$ was −101.8 kcal mol^{-1}. These values led to an estimate of −70 kcal mol^{-1} for $[{}^{\bullet}\text{C-(C}_B\text{)(F)}_2]$.

The second estimate of $[{}^{\bullet}\text{C-(C}_B\text{)(F)}_2]$ required first estimating the value of $[{}^{\bullet}\text{C-(C}_B\text{)(H)(F)}]$. Estimation of the latter value was again performed by two routes. Use of the equation in Table III where X = C_B required the group values, $[{}^{\bullet}\text{C-(H)}_2\text{(F)}]$ and $[\text{C-(H)}_3\text{(F)}]$ (Table II), and $[\text{C-(C}_B\text{)(H)}_2\text{(F)}]$, which was estimated by two routes. Equation 4 and the known value of $[\text{C-(C)(H)}_2\text{(F)}]$ (Table II) gave −51.0 kcal mol^{-1} while eq 5, derived from data in Table V, and a value of −54.0 kcal mol^{-1} [37] for $[\text{C-(C}_d\text{)(H)}_2\text{(F)}]$, gave −53.8 kcal mol^{-1}. The mean value of $[\text{C-(C}_B\text{)(H)}_2\text{(F)}]$

$$[\text{C-(C}_B\text{)(X)(Y)(Z)}] - [\text{C-(C}_d\text{)(X)(Y)(Z)}] = 0.2 \quad (5)$$

was thus −52.4 ± 1.4 kcal mol^{-1}. The first estimate of $[{}^{\bullet}\text{C-(C}_B\text{)(H)(F)}]$ was therefore −21 kcal mol^{-1}. The second estimate of $[{}^{\bullet}\text{C-(C}_B\text{)(H)(F)}]$ employed the equation in Table III where X = F and values of $[{}^{\bullet}\text{C-(C}_B\text{)(H)}_2]$ and $[\text{C-(C}_B\text{)(H)}_3]$ (Table II) and $[\text{C-(C}_B\text{)(H)}_2\text{(F)}]$. This second estimate of $[{}^{\bullet}\text{C-(C}_B\text{)(H)(F)}]$, −22 kcal mol^{-1}, is in good agreement with the first estimate, mean value −21.4 ± 0.4 kcal mol^{-1}. This agreement in estimated values of $[{}^{\bullet}\text{C-(C}_B\text{)(H)(F)}]$ by two different routes provides added confidence that the estimated value is probably near the true value.

The second estimate of $[{}^{\bullet}\text{C-(C}_B\text{)(F)}_2]$ can now be made from the estimated values of $[{}^{\bullet}\text{C-(C}_B\text{)(H)(F)}]$, $[\text{C-(C}_B\text{)(H)(F)}_2]$, and $[\text{C-(C}_B\text{)(H)}_2\text{(F)}]$. The result, −68 kcal mol^{-1} is in reasonable agreement with the first estimate, mean value −69.4 ± 1.0 kcal mol^{-1}.

The only other group value required to complete the estimation of the bond dissociation energies in Table IV is $[\text{C-(C)(C}_B\text{)(F)}_2]$. Equation 4 and the value of $[\text{C-(C)}_2\text{(F)}_2]$, −99 kcal mol^{-1},[1d] gave −98 kcal mol^{-1}.

As far as we are aware, no experimental values for any of the bond dissociation energies in Table IV have been reported. The weakest bond in $PhCF_3$ is apparently the C_B–C bond, calculated value 108.9 kcal mol^{-1}, based on enthalpies of formation of 77.7,[8] −112.0 (Table II), and −143.2[25] kcal mol^{-1} for $Ph^{\bullet}$, ${}^{\bullet}CF_3$, and $PhCF_3$, respectively. Based on an activation energy for the thermolysis of $PhCF_3$ to $Ph^{\bullet}$ and ${}^{\bullet}CF_3$ of 99.7 kcal mol^{-1},[38] the enthalpy of ac-

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tivation for this process is 99.1 kcal mol^{-1} at 25 °C, appreciably less than the calculated value.

An instructive comparison with the results in Table IV are the bond dissociation energies of the corresponding hydrocarbons (Table VI), for which all of the group values required for the calculation of $D(PhCH_2\text{–}R)$ were available.[1d,8] The agreement between the estimated and experimental values for these hydrocarbons is quite good. The large difference between the bond dissociation energies of the first member of each series is of course caused mainly by the intrinsic difference in C–F and C–H bond strengths. As the side chain is lengthened, the differences between the two series decreases until at the propylbenzene stage relatively little difference remains.

In summary, we have shown that within rather broad limits a correlation exits between the differences in group enthalpies of formation for radicals $\{[{}^\bullet C\text{-}(X)(Y)(Z)] - [{}^\bullet C\text{-}(H)(Y)(Z)]\}$ and for molecules $\{[C\text{-}(H)(X)(Y)(Z)] - [C\text{-}(H)_2(Y)(Z)]\}$ and that this correlation can be used for estimating new group values when the other three group values in the set are known or can be estimated. A better correlation exists in some cases if it is limited to only one X group. These correlations should be useful in cases where enthalpies of formation are unavailable.

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Registry No. $PhCF_3$, 98-08-8; $PhCF_2CF_3$, 309-11-5; $PhCF_2CF_2CF_3$, 378-98-3.

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Experimental and Computational Evidence Indicating That the Initial Carbene Conformation Is Product Determining in the Reactions of Cyclopropylmethylene

Jun-Hong Chou, Michael L. McKee,* James De Felippis, Michael Squillacote,* and Philip B. Shevlin*

Department of Chemistry, Auburn University, Auburn University, Alabama 36849

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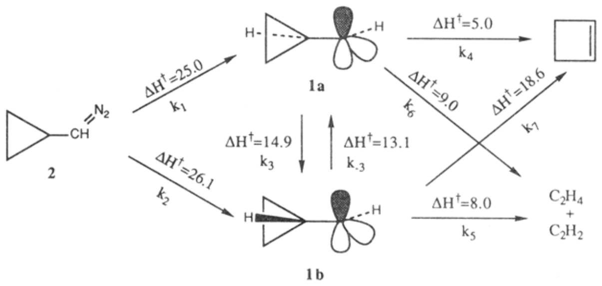
The decomposition of cyclopropyldiazomethane, **2**, to generate cyclopropylmethylene, **1**, was carried out from 573 to 773 K under flash vacuum pyrolysis (FVP) conditions and from 77 to 303 K photolytically in hydrocarbon solvents. An examination of the ratio of ring-expanded products (RE, butadiene and cyclobutene) to those of cleavage (C, ethylene and acetylene) as a funciton of temperature leads to the conclusion that RE is favored over C by 2.3 kcal/mol in the FVP of **2**. Ab initio calculations (MP2/6-31G*//3-21G) predict that decomposition of **2** to give the conformer of **1** in which the ring methyne hydrogen and the α-hydrogen are cis (**1a**) is more favorable than formation of the trans conformer (**1b**) by 1.1 kcal/mol. The calculated activation parameters for the formation of **1a** and **1b** have been combined with those calculated previously for the reactions of **1a** and **1b**, which indicate the RE is favored from **1a** while **1b** gives C, to give theoretical values of RE:C as a function of temperature which lead to a computed difference in E_a between RE and C of 2.7 kcal/mol, in good agreement with the 2.3 kcal observed experimentally. Photolysis of **2** gives a higher ratio of C to RE than does FVP. This may be a consequence of the fact that a more energetic carbene is produced in the photolysis than in the thermolysis.

The reactions of cyclopropylmethylene, **1**, are interesting in that this carbene does not undergo the 1,2-hydrogen migration common to most carbenes with β-hydrogens. Instead, the strain of the cyclopropane ring and the conformation of the carbene dictate rearrangement via a C–C insertion to give cyclobutene and an unusual cleavage of two β C–C bonds to generate ethylene and acetylene.[1,2] Theoretical work has indicated that **1** exists in the two conformations, **1a** (cis) and **1b** (trans) (Scheme I), in which the empty p orbital on the carbene carbon is stabilized by electron donation from the antisymmetric Walsh orbital of the ring.[3-6] In a recent computational investigation of this interesting carbene, we have predicted that **1a** is likely to ring expand to cyclobutene ($k_4 > k_6$) while the most favorable reaction of **1b** is expected to be cleavage to ethylene and acetylene ($k_5 > k_7$, Scheme I).[4] Since these calculations indicate that the barrier to the interconversion of **1a** and **1b** is higher than the respective rates of ring expansion (RE, $k_4 > k_3$) and cleavage (C, $k_5 > k_{-3}$), we have proposed that RE:C ratio in **1** is dictated by the conformation in which the carbene finds itself at birth.[7]

Scheme I



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(7) A rate constant[8] of 9×10^5 s^{-1} and activation energy of 7.4 kcal/mol[9] for the ring expansion of cyclopropylchlorocarbene have recently been measured.

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