a value of ΔE(S–T) at least 5 kcal/mol above both experiment[23] and higher level theoretical studies.[24,25]

Evidence directly conflicting with that of SIBG concerning the heat of formation of methylsilylene, and indirectly supporting a lower value for the energy difference between $H_2Si{=}CH_2$ and SiHMe, comes from a recent kinetic study of decomposition reactions of various methylated disilanes by Walsh.[26] Therein, he provides evidence to support a value of ΔH_f°(SiHME) = 43.9 ± 3 kcal/mol, compared to 53 ± 4 kcal/mol found by SIBG. Combined with Walsh's earlier estimate[3] for the heat of formation of $H_2Si{=}CH_2$, $\Delta H_f^\circ = 39$ kcal/mol, one can infer an energy difference of about 5 kcal/mol, in agreement with our high-level ab initio results.

SIBG also estimated the Si=C π-bond energy in silaethene by calculating the internal rotation barrier. Unfortunately, these authors incorrectly assumed coplanarity of the $CSiH_2$ moiety in the twisted structure, leading to a rotational barrier that is too high by 23 kcal/mol.[27]

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Heats of Formation of Alkyl Radicals from Appearance Energies

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Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5. *Received March 7, 1988*

Abstract: Heats of formation of alkyl radicals have been measured by monoenergetic electron impact on 24 selected precursor molecules as follows: ethyl 27.8; *n*-propyl 22.7; *sec*-propyl 19.1; *n*-butyl 18.1; *sec*-butyl 15.3; isobutyl 15.8; *tert*-butyl 9.5; and neopentyl 10.1 (all kcal mol^{-1}). These values are in good agreement with results from equilibrium measurements using ESR spectroscopy.

Recent investigations show that the heats of formation of C_2–C_4 alkyl radicals, and consequently the strength of C–H bonds in alkanes, are appreciably higher than the values accepted earlier. A revision of $\Delta H_f[C_2H_5^\bullet]$ upward from 25.9[1] to 28.0 kcal mol^{-1},[2] in good agreement with two recent values of 28[3] and 28.4 kcal mol^{-1},[4] has removed inconsistencies associated with the earlier value. The largest remaining disagreements among the ΔH_f data are for *s*-Pr and *t*-Bu radicals; recent values for the former are 22.3,[5] 19.0,[6] and 19.2[2] kcal mol^{-1}, and for the latter 12.4,[5] 9.0,[6] 9.1,[7] 9.2,[8] and 9.4[2] kcal mol^{-1}. For both radicals, the heats of formation, derived by Tsang[5] from his own work and a critical survey of the literature, are about 3 kcal mol^{-1} higher than others recently derived. The consequences of this discrepancy has been commented upon by McMillen and Golden.[1]

In a recent study by Castelhano and Griller,[2] using equilibrium constants for the system

$$CH_3^\bullet + RI \rightleftharpoons CH_3I + R^\bullet$$

measured by electron paramagnetic resonance spectroscopy, heats of formation of the following alkyl radicals have been reported: C_2H_5 28.0, *n*-Pr 22.8, *s*-Pr 19.2, *s*-Bu 15.0, c-pentyl 25.1, *t*-Bu 9.4 kcal mol^{-1}. From these data the authors proposed C–H bond dissociation energies in alkanes as follows: primary C–H ~100, secondary C–H ~96, and tertiary C–H ~94 kcal mol^{-1}.

In view of the fundamental importance of these bond dissociation energies to experimental and theoretical kinetics, we have measured the heats of formation of C_2–C_4 alkyl radicals by an independent method, using the appearance energy (AE) for the ionic reaction:

$$R_1R_2 + e \rightarrow 2e + R_1^+ + R_2^\bullet$$

$$AE[R_1^+] \geq \Delta H_f[R_1^+] + \Delta H_f[R_2^\bullet] - \Delta H_f[R_1R_2]$$

in which the compound R_1R_2 is chosen such that $\Delta H_f[R_1^+]$ is a well-established value, and that $\Delta H_f[R_1R_2]$ is either known experimentally or can be calculated accurately. Recent work in these laboratories has shown that this method can give good values for the heats of formation of radicals and other neutral species[9-14] provided that certain conditions are met which reduce the inequality in the above equation to near zero; i.e., the ionic reaction

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Table I. Appearance Energies and ΔH_f for Ethyl Radical

		ΔH_f (kcal mol^{-1})	
reaction	AE (V)	counterion	radical
$\mathrm{EtCH_2OH} \rightarrow \mathrm{Et^{\bullet}} + [\mathrm{CH_2OH}]^+$	11.20	169[a]	28.1
$\mathrm{EtCH(CH_3)OH} \rightarrow \mathrm{Et^{\bullet}} + [\mathrm{CH_3CHOH}]^+$	10.22	139[b]	26.7
$\mathrm{EtC(CH_3)_2OH} \rightarrow \mathrm{Et^{\bullet}} + [\mathrm{(CH_3)_2COH}]^+$	9.83	119[a]	28.6
$\mathrm{EtCH(CH_3)NH} \rightarrow \mathrm{Et^{\bullet}} + [\mathrm{CH_3CHNH_2}]^+$	9.10	157[c]	27.8
		av	27.8 ± 0.6[d]

[a] See Appendix, Table XI. [b] Reference 23. [c] Reference 24. [d] 28.0 kcal mol^{-1} in ref 2.

Table II. Appearance Energies and ΔH_f for *n*-Propyl Radical

		ΔH_f (kcal mol^{-1})	
reaction	AE (V)	counterion	radical
n-$\mathrm{PrCH_2NH_2} \rightarrow$ *n*-$\mathrm{Pr^{\bullet}} + [\mathrm{CH_2NH_2}]^+$	9.62	177[a]	22.8
n-$\mathrm{PrCH(CH_3)OH} \rightarrow$ *n*-$\mathrm{Pr^{\bullet}} + [\mathrm{CH_3CHOH}]^+$	10.23	139[b]	22.2
n-$\mathrm{PrCH_2NHCH_3} \rightarrow$ *n*-$\mathrm{Pr^{\bullet}} + [\mathrm{CH_2NHCH_3}]^+$	9.13	166[a]	23.2
		av	22.7 ± 0.4[c]

[a] Reference 24. [b] Reference 23. [c] 22.8 kcal mol^{-1} in ref 2.

Table III. Appearance Energies and ΔH_f for *sec*-Propyl Radical

		ΔH_f (kcal mol^{-1})	
reaction	AE (V)	counterion	radical
i-$\mathrm{PrCH_2NH_2} \rightarrow$ *s*-$\mathrm{Pr^{\bullet}} + [\mathrm{CH_2NH_2}]^+$	9.52	177[a]	18.9
i-$\mathrm{PrCH(CH_3)OH} \rightarrow$ *s*-$\mathrm{Pr^{\bullet}} + [\mathrm{CH_3CHOH}]^+$	10.09	139[b]	18.4
i-$\mathrm{PrC(CH_3)_2OH} \rightarrow$ *s*-$\mathrm{Pr^{\bullet}} + [\mathrm{(CH_3)_2COH}]^+$	9.68	119[c]	20.0
		av	19.1 ± 0.6[d]

[a] Reference 24. [b] Reference 23. [c] See Appendix, Table XI. [d] 19.2 kcal mol^{-1} in ref 2.

Table IV. Appearance Energies and ΔH_f for *n*-Butyl Radical

		ΔH_f (kcal mol^{-1})	
reaction	AE (V)	counterion	radical
n-$\mathrm{BuCH_2NH_2} \rightarrow$ *n*-$\mathrm{Bu^{\bullet}} + [\mathrm{CH_2NH_2}]^+$	9.61	177[a]	17.8
n-$\mathrm{BuC(CH_3)_2OH} \rightarrow$ *n*-$\mathrm{Bu^{\bullet}} + [\mathrm{(CH_3)_2COH}]^+$	9.82	119[b]	18.4
		av	18.1 ± 0.6[c]

[a] Reference 24. [b] See Appendix, Table XI. [c] 17.5 kcal mol^{-1}, using D(*n*-Bu–H) = 100 kcal mol^{-1}, ref 2.

Table V. Appearance Energies and ΔH_f for Isobutyl Radical

		ΔH_f (kcal mol^{-1})	
reaction	AE (V)	counterion	radical
i-$\mathrm{BuCH(CH_3)OH} \rightarrow$ *i*-$\mathrm{Bu^{\bullet}} + [\mathrm{CH_3CHOH}]^+$	10.24	139[a]	15.4
i-$\mathrm{BuC(CH_3)_2OH} \rightarrow$ *i*-$\mathrm{Bu^{\bullet}} + [\mathrm{(CH_3)_2COH}]^+$	9.80	119[b]	16.2
i-$\mathrm{BuCH(CH_3)NH_2} \rightarrow$ *i*-$\mathrm{Bu^{\bullet}} + [\mathrm{CH_3CHNH_2}]^+$	9.09	157[c]	15.8
		av	15.8 ± 0.3[d]

[a] Reference 23. [b] See Appendix, Table XI. [c] Reference 24. [d] 15.5 kcal mol^{-1} assuming D(*i*-Bu–H) = 100, ref 2.

Table VI. Appearance Energies and ΔH_f for *sec*-Butyl Radical

		ΔH_f (kcal mol^{-1})	
reaction	AE (V)	counterion	radical
s-$\mathrm{BuCH_2NH_2} \rightarrow$ *s*-$\mathrm{Bu^{\bullet}} + [\mathrm{CH_2NH_2}]^+$	9.57	177[a]	15.2
s-$\mathrm{BuCH(CH_3)OH} \rightarrow$ *s*-$\mathrm{Bu^{\bullet}} + [\mathrm{CH_3CHOH}]^+$	10.24	139[b]	15.6
s-$\mathrm{BuC(CH_3)_2OH} \rightarrow$ *s*-$\mathrm{Bu^{\bullet}} + [\mathrm{(CH_3)_2COH}]^+$	9.68	119[c]	15.1
		av	15.3 ± 0.2[d]

[a] Reference 24. [b] Reference 23. [c] See Appendix, Table XI. [d] 15.0 kcal mol^{-1} in ref 2.

must be a single-bond rupture and preferably the fragmentation of lowest energy requirement, and the measurement of the threshold with energy-selected electrons[15] should be made under conditions where the source residence time is as long as possible (in this case $\geq 10^{-5}$ s). We have chosen the counterion R_1^+ with these points in view; in most cases the counterion is the base peak in the normal mass spectrum of R_1R_2. The criteria for the successful application of the AE method are discussed elsewhere.[16,17] Provided that the heats of formation of the ion and neutral precursor are well established, the remaining experimental uncertainty lies in the ion dissociation having a significant kinetic shift. This

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Table VII. Appearance Energies and ΔH_f for *tert*-Butyl Radical

reaction	AE (V)	ΔH_f (kcal mol^{-1}) counterion	ΔH_f (kcal mol^{-1}) radical
t-BuCH(CH$_3$)OH → t-Bu$^\bullet$ + [CH$_3$CHOH]$^+$	10.14	139[a]	9.7
t-BuCH$_2$NH$_2$ → t-Bu$^\bullet$ + [CH$_2$NH$_2$]$^+$	9.47	177[b]	9.8
t-BuCH(CH$_3$)NH$_2$ → t-Bu$^\bullet$ + [CH$_3$CHNH$_2$]$^+$	8.97	157[b]	9.5
t-BuCH$_2$N(CH$_3$)$_2$ → t-Bu$^\bullet$ + [CH$_2$N(CH$_3$)$_2$]$^+$	8.59	158[b]	9.1
		av	9.5 ± 0.2[c]

[a] Reference 23. [b] Reference 24. [c] 9.4 kcal mol^{-1} in ref 2.

Table VIII. Appearance Energies and ΔH_f for Neopentyl Radical

reaction	AE (V)	ΔH_f (kcal mol^{-1}) counterion	ΔH_f (kcal mol^{-1}) radical
neo-Pent-CH$_2$NH$_2$ → neo-Pent$^\bullet$ + [CH$_2$NH$_2$]$^+$	9.67	177[a]	9.9
neo-Pent-CH(CH$_3$)OH → neo-Pent$^\bullet$ + [CH$_3$CHOH]$^+$	10.35	139[b]	10.4
		av	10.1 ± 0.3[c]

[a] Reference 24. [b] Reference 23. [c] Corresponds to D(neo-Pent–H) = 102 kcal mol^{-1}.

Table IX. Heats of Formation of Radicals and Molecules (kcal mol^{-1})

			X = H		X = Cl		X = Br		X = I	
R$^\bullet$	ΔH_f[R$^\bullet$]	Δ	ΔH_f[RH]	Δ	ΔH_f[RCl]	Δ	ΔH_f[RBr]	Δ	ΔH_f[RI]	Δ
Me	34.4[a]		−17.9		−19.6		−8.5		3.5	
		−6.6		−2.3		−7.2		−6.3		−5.3
Et	27.8[b]		−20.2		−26.8		−14.8		−1.8	
		−8.7		−4.8		−7.8		−9.0		−7.8
s-Pr	19.1[b]		−25.0		−34.6		−23.8		−9.6	
		−9.6		−7.1		−9.0		−7.8		−7.6
t-Bu	9.5[b]		−32.1		−43.6		−31.6		−17.2	

[a] Reference 2 and 21. [b] This work.

latter gives AE values which are too *high*; the reactions used in the present study were selected to have a very small kinetic shift. Consequently the values derived should be considered as upper (rather than lower) limits.

Experimental Section

The apparatus used has been described.[18,19] Fragment ions were generated in the gas phase by impact of an energy-resolved electron beam from an electrostatic electron monochromator. The appearance energy (AE) of a given ion was determined by detecting the threshold for an ion current at the appropriate mass as the energy of the electron beam was increased in 0.02-eV steps. The energy scale was calibrated against H$_2$O, or, in the case of some amines which generated m/z 18 ions (NH$_4^+$ ions), against Xe.

The compounds used were commercial samples of the highest available purity.

Results and Discussion

The accuracy of these results depends primarily on the reliability of the ancillary thermochemical data: the heats of formation of the parent compounds and the counterions. The ΔH_f data for these are discussed in the Appendix. The ionic dissociation reactions leading to formation of the radicals and counterions, together with the appearance energies (AE), the heats of formation used for the counterions, and the resulting ΔH_f[radical], are given in Tables I–VIII Although the absolute error cannot be less than the errors in the ancillary thermochemical data, the very small spread among the individual values for each radical (see tables) indicates that these errors are unlikely to exceed ±1 kcal mol^{-1}. Within these limits our results are in excellent agreement with those of Griller et al.[2] and support their conclusion that the strengths of primary C–H bonds are 100 kcal mol^{-1} (except CH$_3$–H), secondary C–H bonds 96–7 kcal mol^{-1}, and tertiary C–H bonds 94 kcal mol^{-1}.

The present result for neopentyl radical (Table VIII) corresponds to a C–H bond in neopentane of 102 kcal mol^{-1}, 2 kcal mol^{-1} higher than the C–H bond in ethane. Rabinovitch et al.[19] reported 100 ± 2 kcal mol^{-1} for this bond.

Thermochemical Considerations. The decrease in C–H bond dissociation along the series CH$_4$ to i-C$_4$H$_{10}$ has traditionally been considered as reflecting an increasing stabilization in the series of radicals Me to t-Bu. Rüchardt[20] has pointed out that this reduction in bond strengths is not found for C–X bonds along the corresponding heteroatom series CH$_3$X, C$_2$H$_5$X, s-PrX, t-BuX, where X is, for instance, Cl, Br, and I. He concluded therefore that the decrease along the hydrocarbon series did not represent an increase in the stabilization of the radicals, but resulted from an increase in steric strain in the series of RH molecules.

Griller et al.[21] have investigated this situation further for a large number of X substituents, 29 in all. They found that for some X substituents such as halo atoms, OH, OCH$_3$, and NH$_2$, the C–X bond decreased little or not at all along the radical series, but for others, particularly H, CN, C$_6$H$_5$, and Me$_3$Sn, the decrease was large. Their data did not support the suggestion[22] that this difference in behavior is entirely a function of the electronegativity of X.

The bond dissociation energy is the resultant of the values of three entities:

$$D(\text{R–X}) = \Delta H_f[\text{X}] + \Delta H_f[\text{R}^\bullet] - \Delta H_f[\text{RX}]$$

For a given series of radicals, with X a constant, the bond strength will not change provided that the difference between the two remaining terms does not change. This situation will obtain if the effects of substitution on ΔH_f for the radical and the molecule

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Table X. ΔH_f for Parent Compounds (kcal mol^{-1})

compound	ΔH_f	compound	ΔH_f	compound	ΔH_f
$EtCH_2OH$	-61.0[a]	*n*-$BuCH_2NH_2$	-26.8[b]	*t*-$BuCH_2NH_2$	-31.6[b]
$EtCH(CH_3)OH$	-70.0[a]	$EtC(CH_3)_2OH$	-79.1[a]	*t*-$BuCH(CH_3)OH$	-85.1[b]
$EtCH(CH_3)NH_2$	-25.1[a]	*n*-$BuC(CH_3)_2OH$	-89.1[b]	*t*-$BuCH(CH_3)NH_2$	-40.4[b]
n-$PrCH_2NH_2$	-22.0[a]	*i*-$BuCH(CH_3)OH$	-81.7[b]	*t*-$BuCH_2N(CH_3)_2$	-31.0[b]
n-$PrCH(CH_3)OH$	-74.7[a]	*i*-$BuC(CH_3)_2OH$	-90.8[b]	neo-$PentCH_2NH_2$	-36.1[b]
n-$PrCH_2NHCH_3$	-21.3[b]	*i*-$BuCH(CH_3)NH_2$	-36.8[b]	neo-$PentCH(CH_3)OH$	-89.3[b]
i-$PrCH_2NH_2$	-23.6[a]	*s*-$BuCH_2NH_2$	-28.5[b]		
i-$PrCH(CH_3)OH$	-75.3[a]	*s*-$BuCH(CH_3)OH$	-81.5[b]		
i-$PrC(CH_3)_2OH$	-84.2[b]	*s*-$BuC(CH_3)_2OH$	-89.1[b]		

[a] Reference 25. [b] Calculated by additivity[26] (see text).

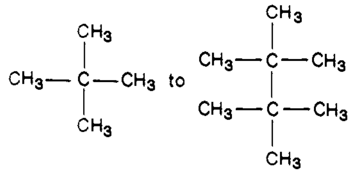
Table XI. Appearance Energies and ΔH_f for $[CH_2OH]^+$ and $[(CH_3)_2COH]^+$

reaction	AE (V) EM	AE (V) PI	ΔH_f[ion] (kcal mol^{-1})
$CH_3OH \rightarrow [CH_2OH]^+ + H^\bullet$	11.69[a]	11.67[b]	169
$CH_3CH_2OH \rightarrow [CH_2OH]^+ + Me^\bullet$	11.30[a]	11.25[b]	169
$(CH_3)_3COH \rightarrow [(CH_3)_2COH]^+ + Me^\bullet$	9.86[a]	9.87[b]	118
$EtC(CH_3)_2OH \rightarrow [(CH_3)_2COH]^+ + Et^\bullet$	9.80[a]		119

[a] Reference 23. [b] Refaey, K. M. A.; Chupka, W. A. *J. Chem. Phys.* **1968**, *48*, 5205.

are the same. Values for this effect are tabulated in Table IX. It can be seen that the sequence of changes in $\Delta H_f[R^\bullet]$ resulting from successive CH_3 substitutions in $R^\bullet$ is nearly the same as for the corresponding substitutions in the halide molecules RX. The result is that $D(R-X)$ changes very little if at all with substitution. By contrast the Δ for the hydrocarbon molecules is much smaller for the first substitution but increases rapidly with further substitution. The result is that $D(R-H)$ decreases rapidly along the series.

This decrease does not appear to arise from steric strain in the larger hydrocarbons, as proposed by Rüchardt,[20] because the Δ steps along the series become progressively *larger*, rather than smaller as would be the case if steric strain were increasing along the series. Griller et al.[21] rightly claim that steric strain is significant in the decrease in $D(C-C)$ in the series



where very bulky groups are involved. However, this argument cannot apply to the smaller systems considered above. Moreover, would not the steric strain in the RX series be at least as large as in the RH series? Very recently Fliszar and Minichino[27] have attempted to describe bond fission in alkanes in greater theoretical detail using the concept that the radical fragments $R_1^\bullet$ and $R_2^\bullet$ may not be individually electroneutral in the host molecule.

Appendix

For the heats of formation of the parent compounds we have used values from the recent compilation by Pedley, Naylor, and Kirby[25] where available; otherwise we have calculated ΔH_f values using the additivity scheme of Benson[26] which has proved to be remarkably reliable. For branched compounds we have applied appropriate gauche corrections. These ΔH_f values are given in Table X.

The values used for $\Delta H_f[CH_2OH]^+$ and $\Delta H_f[(CH_3)_2COH]^+$ are derived from photoelectron (PI) and monoenergetic (EM) impact on appropriate alcohols, as summarized in Table XI.

Registry No. Et$^\bullet$, 2025-56-1; Pr$^\bullet$, 2143-61-5; *s*-Pr$^\bullet$, 2025-55-0; Bu$^\bullet$, 2492-36-6; *i*-Bu$^\bullet$, 4630-45-9; *s*-Bu$^\bullet$, 2348-55-2; *t*-Bu$^\bullet$, 1605-73-8; neo-Pent$^\bullet$, 3744-21-6.

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