Table V, reveal just how well lithium functions in this respect. Since both the CLi_3 radical and the CLi_3^+ cation are highly stabilized, the remarkably low experimental ionization potential of the former, 4.6 ± 0.3 eV, is not a full measure of the carbenium ion stability. Were not the CLi_3 radical so stable, its IP would be even lower.

What is the origin of the remarkable stability of these lithiated species? A carbenium ion is stabilized by a group which increases the electron density at the central carbon atom. Conventionally, only π donors have been considered to be stabilizing because of the formally vacant carbenium ion p orbital. However, σ donors can be just as effective. Increasing the electron density at the charged atom through donation is an efficient mode of stabilization. Interestingly, several α-metallocarbenium ions have been implicated as intermediates in catalytic isomerization reactions.[21] The unusual structures reported for carbenoids have also be rationalized on the basis of ion pairs involving metallocarbenium ions.[22] The stabilization of a radical by lithium can be attributed both to its π acceptor and σ donor abilities.

Our results refer only to the thermodynamic stability of the various species. A discussion of kinetic stability is beyond the scope of the present work. We emphasize that solvation and association are important for these and other lithium compounds. However, the experimental observation in the gas phase of monomeric $CLi_3\cdot$ as well as the cations, CH_2Li^+, and CLi_3^+,[1] is a stimulus for further experimental and theoretical study of organolithium compounds.[23]

Conclusions

The principal conclusions to be drawn from this study are the following:

1. Substitution of hydrogen by lithium in the methyl cation lowers the energy of triplet states more than singlets. CH_2Li^+ is still a ground-state singlet, but with a much reduced singlet–triplet separation compared with CH_3^+. $CHLi_2^+$ and CLi_3^+ are predicted to have triplet ground states.
2. The ionization potential of CLi_3 is predicted to be 6 eV less than that of CH_3, in reasonable agreement with experiment.
3. Lithium is a strong stabilizing substituent for carbenium ions, comparable to π donors such as NH_2. CLi_3^+ is one of the most stable carbenium ions known.

Note Added in Proof. After writing this paper, additional work has revealed the triplet methyl cation (but not its lithiated counterparts) to be nonplanar. This will be discussed in a future publication.

Acknowledgment. We thank Dr. C. H. Wu for his interest, Dr. E. D. Jemmis for early contributions to this work, and Professor R. J. Lagow for information prior to publication. Support was provided by the National Science Foundation (Grant CHE-79-01061-01), a NATO Grant, the Fonds der Chemischen Industrie, and Professor Dr. W. Meyer.

Registry No. CH_3^+, 14531-53-4; $CH_3\cdot$, 2229-07-4; CH_2Li^+, 62581-43-5; $CH_2Li\cdot$, 81506-43-6; $CHLi_2^+$, 81506-44-7; $CHLi_2\cdot$, 81506-45-8; CLi_3^+, 81506-46-9; $CH_2CH_3^+$, 14936-94-8; $CH(CH_3)_2^+$, 19252-53-0; $C(CH_3)_3^+$, 14804-25-2; $CH_2NH_2^+$, 54088-53-8; $CH(NH_2)_2^+$, 50676-76-1; $C(NH_2)_3^+$, 43531-41-5; $CH_2\cdot$, 2465-56-7; $CH_2OH\cdot$, 2597-43-5; $CH_2NH_2\cdot$, 10507-29-6; $CH_2NMe_2\cdot$, 30208-47-0; Li, 7439-93-2; Na, 7440-23-5; Rb, 7440-17-7; Cs, 7440-46-2; $CLi_3\cdot$, 81506-48-1; ethyl, 2025-56-1; 2-propyl, 2025-55-0; *tert*-butyl, 1605-73-8; allyl, 1981-80-2; benzyl, 2154-56-5; diphenylmethyl, 4471-17-4; tropyl, 3551-27-7.

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Heats of Formation of Some Simple Alkyl Radicals[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received October 14, 1981*

Abstract: Equilibrium constants, *K*, for the system $Me\cdot + RI \rightleftarrows MeI + R\cdot$ were measured in solution by using electron paramagnetic resonance spectroscopy. Given the entropies of the components of the equilibrium and the heats of formation of the iodides, the relative heats of formation of the alkyl radicals were obtained. With $\Delta H_{f,300}(Me\cdot) = 34.4$ kcal mol^{-1} chosen as a standard, the following heats of formation for other alkyl radicals were obtained: Et·, 28.0; *n*-Pr·, 22.8; *i*-Pr·, 19.2; *s*-Bu·, 13.9; c-$C_5H_9\cdot$, 25.1; *t*-Bu·, 9.4 kcal mol^{-1}. These data lead to the following C–H bond dissociation energies for simple alkanes: primary C–H, ~100; secondary C–H, ~96; tertiary C–H, ~94 kcal mol^{-1}.

The C–H bond dissociation energies, BDE, in simple alkanes form a vital part of our understanding of the influence of thermodynamic properties on chemical reactivity. Differences in these energies, while small in percentage terms, obviously have a profound influence on the pathways of chemical reactions. They are, nevertheless, notoriously difficult to quantify, as are the related heats of formation of alkyl radicals, $\Delta H_f(R\cdot)$, eq 1. For example,

$$BDE(R-H) = \Delta H_f(R\cdot) + \Delta H_f(H\cdot) - \Delta H_f(R-H) \qquad (1)$$

estimates of the bond dissociation energy for the simplest tertiary C–H bond, i.e., that in isobutane,[2-8] cover the range 91.2–97.4 kcal mol^{-1}. The spread in these values is due entirely to discrepancies in the measured values of $\Delta H_f(t\text{-Bu}\cdot)$.[2-7]

In a preliminary report of this work,[9] we demonstrated that a "radical buffer"[10] system could be used to measure the *relative*

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heats of formation of alkyl radicals. By choosing $\Delta H_f(\mathrm{Me}\cdot) = 34.4 \pm 0.7$ kcal mol^{-1} as a standard,[11] we were able to determine the heats of formation of ethyl and *tert*-butyl radicals and hence the C–H bond dissociation energies in ethane and of the tertiary bond in isobutane. In this work we describe an extension of this study to a series of alkyl radicals.

Experimental Section

Materials. The alkyl iodides used in this work were commerically available. In general, they were purified by washing with a saturated solution of sodium bisulfite followed by drying over anhydrous magnesium sulfate and were then distilled. The distillates were stored at 0 °C over copper turnings. Methyl iodide was distilled from phosphorus pentoxide. Other commerically available materials were used as received.

Di-*tert*-butyl hyponitrite was prepared from *tert*-butyl bromide and silver hyponitrite[13] following the method reported by Kiefer and Traylor.[14] Phenylacetyl peroxide was prepared by a slightly modified version of the method reported by Walling and Lepley.[15] Thus 4 mL (30 mmol) of phenylacetyl chloride in 20 mL of pentane at ~-5 °C was treated with 3.5 mL (30 mmol) of cold 30% H_2O_2 with constant stirring. A cold solution of 6.4 mL (160 mmol) of NaOH in 30 mL of water was then added dropwise and the peroxide precipitated out of the solution. Ten minutes after the addition, the precipitate was filtered in the cold and dried under high vacuum (temperature maintained under −10 °C). An iodometric determination of peroxide was carried by dissolving 100 mg of peroxide in chilled, nitrogen-purged, glacial acetic acid (15 mL) containing 1 g of sodium iodide. The liberated iodine was then titrated with a 1.0 M sodium thiosulfate solution. The peroxide was ~90% pure and was obtained in yields better than 70%.

EPR Measurements. Electron paramagnetic resonance, EPR, experiments were carried out with a Varian E104 spectrometer. Thermolysis and photolysis were used for radical generation. The photolysis source was a 500-W high-pressure mercury arc lamp, and the output of the lamp was filtered by using an aqueous cobalt–nickel sulfate filter solution, which removed most of the visible and infrared radiation. After filtration the heating effect at the sample due to the lamp was less than 1 °C.

Typically samples for thermolysis were prepared in isooctane solution (0.5 mL) and contained di-*tert*-butyl hyponitrite (50 mg; 0.57 M), triphenylarsine (90 mg; 0.5 M) or triphenylboron (~0.4 M; saturated solution prepared under N_2), and two alkyl iodides (0.1–2.0 M), reactions 2–8. The mixture was degassed by three freeze–pump–thaw cycles. To prevent boiling, the pressure within the tube was set at 10 mmHg by back-filling with N_2 before it was sealed. The mixture was heated at 60 °C in the spectrometer cavity, and the spectra due to the two alkyl radicals were recorded.

In photolysis experiments di-*tert*-butyl hyponitrite and triphenylarsine or triphenylboron were replaced by hexamethylditin (0.1 mL, 0.6 M), eq 9 and 10.

NMR Measurements. Some nuclear magnetic resonance, NMR, experiments were carried out on systems involving benzyl radicals to test for chemically induced dynamic nuclear polarization, CIDNP, effects. Solutions were prepared in benzene-d_6 (0.5 mL) containing phenylacetyl peroxide (60 mg, 0.44 M), alkyl halide (~0.4 M), and tetramethylsilane as an internal reference. The solutions were prepared at 0 °C and were placed in the probe of a Bruker WP-80 Fourier transform spectrometer that had been prehated to 43 °C. Proton spectra were recorded every 30 s for 4 min, after which time the peroxide had largely decomposed.

Thermochemical Measurements. A number of experiments were carried out in order to measure the heats of reactions in solution of a variety of alkyl iodides with tri-*n*-butyltin hydride. A simple calorimeter was assembled for this purpose and consisted of a covered Dewar fitted with the following: (a) a thermistor, which was used to monitor temperature changes (b) a magnetic stirrer, (c) a resistor, which was used to calibrate the calorimeter electrically, and (d) a coil of glass tubing through which air could be blown to cool and reequilibrate the system. The Dewar assembly was immersed in a thermostated water bath (27.0 ± 0.1 °C).

In a typical experiment, the Dewar was charged with isooctane (40 mL), which was then degassed by nitrogen purging. Tri-*n*-butyltin hydride (2 mL) was then added together with a thin-walled glass ampule containing a carefully measured quantity of an alkyl iodide (ca. 80 mg) in isooctane (0.5 mL). The system was allowed to reach thermal equilibrium. The ampule was then crushed, releasing the iodide, and an exothermic reaction began immediately and was complete in ca. 5 min, eq 11. A thermogram was obtained by plotting the change in the resistance of the thermistor with time. After reaction the calorimeter and contents were easily restored to the starting temperature by sweeping air through the heat exchanger coil. The heat capacity of the system was then calibrated by heating electrically with the resistor. The power applied was adjusted until the calibration thermogram was essentially identical with that produced in the chemical reaction. The mismatching of thermograms from reaction and calibration was the most important source of experimental error. Three measurements of the heat of reaction were carried out for each iodide.

Results and Discussion

Radical Buffer. In this work we have made use of a radical buffer system to measure the equilibrium constants, *K*, for the rapid exchange reactions that take place between alkyl radicals and alkyl iodides, eq 5. Given the entropies of the components involved in the equilibrium and the heats of formation for the alkyl iodides, the *relative* heats of formation of the two alkyl radicals were obtained. By choosing $\Delta H_f(\mathrm{Me}\cdot)$ as a standard,[11] it was possible to assign absolute values to all $\Delta H_f(\mathrm{R}\cdot)$.

The use of a radical buffer in this context is in sharp contrast with its original application in the pioneering work of Hiatt and Benson.[10] These authors used "known" thermochemistry to compute *K* and hence to establish the relative concentrations of alkyl radicals present in gas-phase systems. As a result of the logarithmic relationship between *K* and ΔG, small uncertainties in the thermochemical parameters led to very large errors in *K*. However, in this work we have reversed the approach and have measured values of *K* by directly monitoring the alkyl radicals with EPR spectroscopy. The experimental errors are such that ΔG can be determined accurately.

Radicals were generated at 60 °C in the EPR cavity according to the reaction scheme shown in eq 2–8 (M ≡ As, B). Relative

$$t\text{-BuO—N}{=}\text{N—OBu-}t \rightarrow 2t\text{-BuO}\cdot + \mathrm{N_2} \tag{2}$$

$$t\text{-BuO}\cdot + \mathrm{Ph_3M} \rightarrow t\text{-BuOMPh}_2 + \mathrm{Ph}\cdot \tag{3}$$

$$\mathrm{Ph}\cdot + \mathrm{RI/R'}\cdot \rightarrow \mathrm{PhI} + \mathrm{R}\cdot/\mathrm{R'}\cdot \tag{4}$$

$$\mathrm{R}\cdot + \mathrm{R'I} \overset{K}{\rightleftharpoons} \mathrm{RI} + \mathrm{R'}\cdot \tag{5}$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \rightarrow \text{nonradical products} \tag{6}$$

$$\mathrm{R}\cdot + \mathrm{R'}\cdot \rightarrow \text{nonradical products} \tag{7}$$

$$\mathrm{R'}\cdot + \mathrm{R'}\cdot \rightarrow \text{nonradical products} \tag{8}$$

radical concentrations were obtained by double integration of appropriate lines in the spectra of R· and R′·, which were repeatedly recorded. Extrapolation of these data to the start of the experiment gave the relative radical concentrations at a point where the concentrations of the iodides were known precisely.

An alternative photolytic method for radical generation was also used at 0 °C so as to provide a double check on measurements of *K*, eq 9 and 10. In experiments involving methyl radicals there

$$\mathrm{Me_3SnSnMe_3} \xrightarrow{h\nu} 2\mathrm{Me_3Sn}\cdot \tag{9}$$

$$\mathrm{Me_3Sn}\cdot + \mathrm{RI/R'I} \rightarrow \mathrm{Me_3SnI} + \mathrm{R}\cdot/\mathrm{R'}\cdot \tag{10}$$

was some evidence that methyl was abstracting hydrogen from the solvent, and hence only the low-temperature photolytic data were used in this case.

Two conditions must be fulfilled in order to calculate values of *K* from these results. First, the reaction of phenyl radicals with alkyl iodides, eq 4, must be essentially irreversible. Second, the reactions of alkyl radicals with alkyl iodides must be faster than the reactions that remove radicals from the system, eq 6–8.

There is a good deal of evidence in the literature that supports these two requirements, and it is largely based upon CIDNP

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Table I. Values of K for Reaction 5

	R·					
R'·	Me·	Et·	n-Pr·	i-Pr·	s-Bu·	t-Bu·
Et·	23.5[a]					
n-Pr·	14.6[b]	0.54[b]				
i-Pr·		21.5[a]	32.5[b]			
s-Bu·		12.4,[c] 12.0[a]		0.54[c]		
t-Bu·				21.7,[c] 18.0[b]	36.0[c]	
c-C_5H_9·		20.4,[c] 17.2[d]	27.0[b]	0.87[c]	1.4[c]	0.038[c]

[a] Photolytic method at 0 °C. [b] Photolytic method using a flow system at 25 °C. [c] Thermolytic method using Ph_3As. [d] Thermolytic method using Ph_3B.

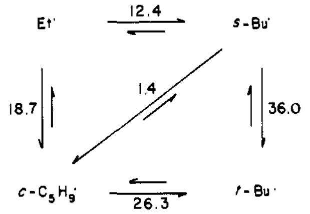
studies. For example, when lauryl peroxide is thermolyzed in the presence of iodobenzene, 1-undecyl iodide is not formed nor is there polarization in the proton spectrum of iodobenzene, indicating that the n-alkyl radical does not react significantly with iodobenzene.[16,17] This supports the premise that the reaction of phenyl radicals with alkyl iodides is essentially irreversible. By contrast iodine exchange between alkyl radicals and alkyl iodides is an efficient and reversible process, as evidenced by the transfer of polarization in CIDNP experiments. Such experiments suggest that the rate constants for these transfers must be $>10^5$ M^{-1} s^{-1}.[16-19] Hence, under our experimental conditions where radical concentrations were ca. 10^{-8} M, the rate of the exchange process was at least 100 times greater than the rates at which radicals were being removed from the system by self-reactions 6-8. It should be noted that these observations apply to radicals that are not highly stabilized. For allyl and benzyl the exchange process was in fact far less efficient than the self-reactions of these radicals (vide infra).

Measurements of K. Values of K obtained by using the radical buffer systems were independent of both the relative and absolute concentrations of the two iodides when these were varied by a factor of 10. Each value of K was based upon the results of two to five experiments. The values obtained are shown in Table I. The main source of experimental error in these data arose from errors in double integration of the EPR signals.

For each radical, buffer systems were set up so as to allow comparison with at least two others. However, there were experimental limitations on the extent to which such comparisons could be made. For example, methyl could only be compared against n-alkyl radicals because of the magnitudes of K for other cases. In addition, overlap in the EPR spectra precluded a number of experiments with the notable exception of comparisons with cyclopentyl for which line overlap with other alkyls was a far less severe problem.

When data for K were avabilable at two different temperatures, values of K_{300} were obtained by interpolation. In other cases temperature corrections to K were made by using the heat capacities and entropies of the components in the equilibrium.[10c,20] In general, such corrections were small. The corrected values of K are shown in Table II. Buffer systems involving Me·, Et·, or n-Pr· were chosen as standards. Other systems were used to check the internal consistency of the data at a given temperature. An example of this method is shown in Scheme I.

Scheme I



Values obtained for K_{300} are quite different from those which would be expected if the rates for the equilibrium reactions, eq 5, were slow compared to the rates of self-reaction of the radicals, eq 6-8. Under this condition values of "K" would not represent an equilibrium constant but would be equal to the relative rates of iodine abstraction from RI and R'I by either phenyl or stannyl radicals. Table III shows that, in general, this is not the case and supports the use of the buffer system in this context.

Limitations of the System. Several experiments were carried out in an attempt to establish the heats of formation of allyl and benzyl radicals. Since both of these radicals have high stabilization energies, the use of their parent iodides in radical buffer systems with alkyl iodides was inappropriate because of the very large values of K that would result. Accordingly, benzyl and alkyl bromides were used in their place.

In experiments designed to set up buffers for $tert$-butyl or isopropyl radicals with allyl or benzyl, the cross-multiplication method of validating the data (see Scheme I, for example) consistently failed, and the discrepancies between the "K" consistently failed, and the discrepancies between the "K" values were often greater than an order of magnitude. The failure was not due to accumulation of allyl or benzyl iodides in these systems since experiments in which the solutions were flowed trhough the EPR cavity or in which the initiating light intensity was reduced to 10% of its original value had no effect on the results. This suggested that rapid exchange was not being achieved in the buffer systems.

CIDNP experiments[17] in which aliphatic diacyl peroxides were thermolyzed in the presence of 3-bromopropene show that bromine abstraction by n-alkyl radicals is sufficiently rapid for use in this work. We therefore concluded that the reactions of allyl and benzyl radicals with the alkyl iodides used must have been too slow for the buffer to be established. To confirm this view we thermolyzed in an NMR probe solutions of phenylacetyl peroxide in benzene-d_6, which contained either bromotrichloromethane, 3-bromopropene, isopropyl iodide, or $tert$-butyl iodide. Only bromotrichloromethane gave rise to polarization effects as has been previously reported.[15] In all other cases, the reactions of benzyl radicals formed in the peroxide thermolyses with the other substrates must have been too slow for polarization transfer and hence were unsuitable for the radical buffer technique.

Calculation of $\Delta H_{f,300}(R\cdot)$. Values of $\Delta H_{f,300}(R\cdot)$ were calculated from K_{300} by using literature data for the thermodynamic properties of the components of the buffer system, Table II. Some comments on these data are appropriate since they form an important component of this work.

In general, the data used for $S^\circ_{300}(R\cdot)$ were those obtained by Purnell and Quinn,[22] which take proper account of vibrational contributions[23] to entropy. In particular, they make use of a "reduced-mass dependence" for the out-of-plane vibrational frequencies for R·, an approach that was subsequently validated by experiment.[24] The value for $S^\circ_{300}(t\text{-Bu}\cdot) = 73$ cal deg^{-1} mol^{-1} was calculated by Lewis and Benson[25] and was based upon experimentally determined values for the vibrational frequencies of $tert$-butyl.[23,26,27] However, calculations by Pacansky and Chang[27] based on the same experimental data gave a value of $S^\circ_{300}(t\text{-Bu}\cdot)$

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Table II. Thermodynamic Parameters Used in the Calculation of $\Delta H_{f,300}(R\cdot)$[a]

$R'\cdot$	K_{300}[b]	$S°_{300}(R'\cdot)$[a]	$S°_{300}(R'I)$	$\Delta H_{f,300}(R'I)$	$\Delta H_{f,300}(R'\cdot)$	BDE(R'–H)
Me·	1.0	46.4[c]	60.5[d]	3.4[e]	34.4[f]	104.4
Et·	20.1	59.2[c]	70.7[g]	−2.0[e]	28.0[h]	100.3
n-Pr·	14.6	69.4[c]	81.0[i]	−7.4[i]	22.8[j]	99.7
i-Pr·	468	67.7[c]	77.6[i]	−9.4[i]	19.2[k]	96.1
s-Bu·	245	77.6[l]	88.5[m]	−14.8[n]	13.9	96.4
c-$C_5H_9\cdot$	394	74.6[p]	86.5[p]	−2.96[p]	25.1[p]	95.6
t-Bu·	1.67×10^4	73.0[q]	82.5[r]	−17.2[d]	9.4[s]	93.9

[a] ΔH_f, kcal mol^{-1}; $S°$, cal deg^{-1} mol^{-1}. [b] For reaction 5, R ≡ Me. [c] Reference 22. [d] Gelles, E.; Pitzer, K. S. *J. Am. Chem. Soc.* 1953, *75*, 5259–5267. [e] Reference 8. [f] Reference standard.[11] [g] Benson, S. W.; Amano, A. *J. Chem. Phys.* 1962, *36*, 3464–3471. [h] Literature value: reference 7. [i] Furuyama, S.; Golden, D. M.; Benson, S. W. *J. Chem. Thermodynamics* 1969, *1*, 363–375. [j] Literature value: Marshall, R. M.; Rahman, L. *Int. J. Chem. Kinet.* 1977, *9*, 705–724. [k] Literature value: reference 21. [l] O'Neal, H. E.; Benson, S. W. *Int. J. Chem. Kinet.* 1969, *1*, 221–243. [m] Calculated from group contributions.[20] [n] From group contributions;[20] see also: Traeger, J. C. *Org. Mass. Spectrometry* 1981, *16*, 193–194. [o] Literature value: Marshall, R. M.; Page, N. D. *Int. J. Chem. Kinet.* 1979, *11*, 199–215. [p] Reference 28. [q] Reference 25. [r] Benson, S. W.; Amano, A. *J. Chem. Phys.* **1962**, *37*, 197–198. [s] Literature values: ref 4, 6, 7, 30, and 31.

Table III. Relative Rates of Halogen Abstraction by Phenyl and Tri-*n*-butylstannyl Radicals

Ph·		*n*-$Bu_3Sn\cdot$	
RI	rel react	RI	rel react
MeI	1.0	MeI	1.0
EtI	1.9	CH_2CHCH_2Br	0.24
i-PrI	3.4	$PhCH_2Br$	0.26
s-BuI	3.2		
t-BuI	6.4		

Table IV. Heats of Reaction, ΔH, for the Reduction of Alkyl Iodides by Tri-*n*-butyltin Hydride

RI	$-\Delta H$,[a] kcal mol^{-1}	$\Delta H_{f,300}(RI)$,[b] kcal mol^{-1}
MeI	44.72 ± 0.72	3.4
EtI	40.40 ± 0.54	−3.3 ± 1.3
i-PrI	40.51 ± 0.20	−7.8 ± 1.0
s-BuI	40.12 ± 0.76	−13.7 ± 1.6
c-C_5H_9I	39.84 ± 0.56	−2.0 ± 1.4
t-BuI	39.14 ± 0.64	−16.7 ± 1.4

[a] Errors quoted represent one standard deviation. [b] Thermochemical data for $\Delta H_{f,300}(RI)$ taken from ref 8.

= 76 cal deg^{-1} mol^{-1}. The difference between the two approaches rests upon assumptions about the barrier for asymmetric rotation of the methyl groups in *tert*-butyl.

It should be noted that the literature values used for calculations on the cyclopentyl radical were all derived in an experiment to measure $\Delta H_f(c\text{-}C_5H_9\cdot)$;[28] hence there is an obvious circularity in their use in this context. However, the fact that two quite different experiments establish the same relationships within experimental error between the free energy of the cyclopentyl radical and its parent iodide is of significance.

Literature data for the heats of formation of alkyl iodides were checked in this work by measuring heats of reactions for the reductions of RI by tri-*n*-butyltin hydride, eq 11. Although these

$$n\text{-}Bu_3SnH + RI \rightarrow n\text{-}Bu_3SnI + RH \qquad (11)$$

measurements were carried out in solution, they can be regarded as being equivalent to gas-phase data to a good approximation (vide infra). The results obtain yield relative values for $\Delta H_{f,300}(RI)$; absolute values were derived by taking $\Delta H_{f,300}(MeI) = 3.4$ kcal mol^{-1} as a standard.[8] The data are given in Table IV and are in good agreement with previously published results, implying that the literature values for $\Delta H_{f,300}(RI)$ can be used with confidence.

The values of K and of $\Delta H_f(RI)$ obtained in this work were measured in solution. However, if we assume that the free energies of vaporization and mixing of the radicals concerned are similar to those of their parent hydrocarbons, we can treat these data as being equivalent to gas-phase results. The reason for this is broadly that hydrocarbons and alkyl iodides are not strongly solvated in hydrocarbon solution. More explicitly, the heats of mixing of these compounds with hydrocarbon solvent are small (<100 cal mol^{-1}),[29] and since we are dealing with differences in the heats of mixing of the components of the buffer systems, these contributions are negligible. Moreover, corrections to the free energies of the radicals and alkyl iodides for vaporization are subject to the "compensation effect". This effect has been discussed in detail elsewhere[20] and establishes that the enthalpy and entropy changes involved are approximately equal in magnitude and opposite in sign.

The experimental errors associated with values of $\Delta H_{f,300}(R\cdot)$ stem mostly from uncertainties in $\Delta H_{f,300}(RI)$. When an additional contribution of ±1 cal deg^{-1} mol^{-1} is allowed for ΔS for the equilibrium systems, a total experimental error of ca. ±1 kcal mol^{-1} results. Errors in the measured values of K_{300} do not contribute significantly since they are small in magnitude and are logarithmically related to the thermodynamic parameters of interest.

Comparisons with Literature Data. The results obtained in this work for $\Delta H_{f,300}(R\cdot)$ yield the following values for the C–H bond dissociation energies in alkanes: primary C–H, ~100 kcal mol^{-1}; secondary C–H, ~96 kcal mol^{-1}; and tertiary C–H ~94 kcal mol^{-1}. The individual results for $\Delta H_{f,300}(R\cdot)$ are generally in excellent agreement with the most recent literature data but conflict with the normally accepted values for ethyl and *tert*-butyl.

The value of $\Delta H_{f,300}(Et\cdot)$ obtained in this work is higher than the generally accepted value of 25.9 ± 1.3 kcal mol^{-1}.[21] However, this higher value has the effect of reconciling currently conflicting gas-phase data[6,7,10a] such as those on the kinetics for self-reaction of ethyl.[6,10a] This enhances our confidence in its accuracy and lends support to a value of 100 kcal mol^{-1} for the C–H bond dissociation energy vs. the normally accepted value of 98 kcal mol^{-1}.

The value for the heat of formation of *tert*-butyl obtained in this work is in good agreement with the results of several recent determinations that give $\Delta H_{f,300}(t\text{-}Bu\cdot) = 8.4\text{–}10.5$ kcal mol^{-1}. All of these results set $\Delta H_{f,300}(t\text{-}Bu\cdot)$ ~2 kcal mol^{-1} higher than the normally accepted value and thus lead to a similar increase in the bond dissociation energy of the tertiary C–H bond. Since our value falls at the mean of the most recent results, we recommend its use until more accurate methods of measurement become available.

Summary

The majority of methods to measure $\Delta H_f(R\cdot)$ are based upon studies of chemical reactions that relate this quantity to the thermodynamic properties of other molecules and atoms that are accurately known. In this work we have established a network of relationships that interlink the thermodynamic properties of

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(28) Furuyama, S.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1970**, *2*, 83–92.

(29) Wisniak, J.; Tamir, A., "Mixing and Excess Thermodynamic Properties"; Elsevier: New York, 1978.

(30) $\Delta H_{f,300}(t\text{-}Bu\cdot) = 9 \pm 1$ kcal mol^{-1}: Lossing F. P., private communication.

(31) Canosa, C. E.; Marshall, R. M. *Int. J. Chem. Kinet.* **1981**, *13*, 303–316.

simple alkyl radicals and their parent iodides. The strength of the method is that a series of related experiments yield a complete set of values for $\Delta H_{f,300}(R\cdot)$. Its weakness is that it relies upon thermodynamic data drawn from the literature. Despite the weakness in this technique, it is clear that our measurements of K_{300} adequately characterize the properties of the radical buffer systems and can always be used to recompute values of $\Delta H_f(R\cdot)$ as thermodynamic data for properties such as $S°(R\cdot)$ are revised.

The approach used in this work, in common with all other methods currently available, yields measurements of $\Delta H_f(R\cdot)$ and BDE(R–H), which are subject to fairly high limits of error. At present, it seems that the only way in which such values can be refined is by combination and comparison of results from a variety of experiments that effectively define acceptable ranges for these quantities.

Our results and those of other recent studies in this field suggest that the most satisfactory estimates of bond dissociation energies in alkanes currently available are the following: primary C–H bond, ~100 kcal mol^{-1}; secondary C–H bond, ~96 kcal mol^{-1}; tertiary C–H bond, ~94 kcal mol^{-1}.

Acknowledgment. We thank Drs. S. W. Benson and J. C. Traeger for helpful comments and suggestions.

Registry No. Et·, 2025-56-1; *n*-Pr·, 2143-61-5; *i*-Pr·, 2025-55-0; *sec*-Bu·, 2348-55-2; *t*-Bu·, 1605-73-8; *c*-C_5H_9·, 3889-74-5; Me·, 2229-07-4; Ph·, 2396-01-2; *n*-Bu_3Sn·, 20763-88-6; MeI, 74-88-4; EtI, 75-03-6; *i*-PrI, 75-30-9; *sec*-BuI, 513-48-4; *t*-BuI, 558-17-8; CH_2CHCH_2Br, 106-95-6; $PhCH_2Br$, 100-39-0; *c*-C_5H_9I, 1556-18-9; tri-*n*-butyltin hydride, 688-73-3; phenylacetyl peroxide, 19910-09-9.

Competitive [6 + 2], [4 + 2], and [2 + 2] Cycloadditions. Experimental Classification of Two-Electron Cycloaddends

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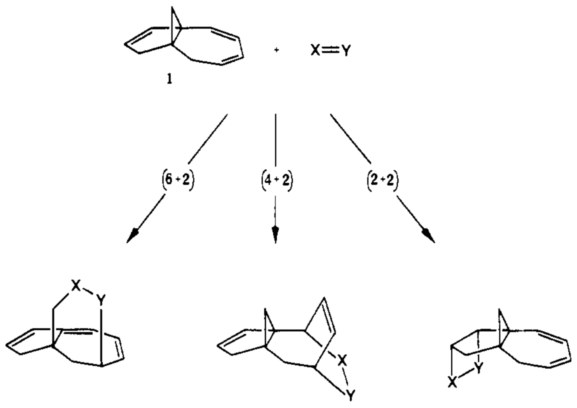
Abstract: Seven common electron-deficient $_\pi2$-cycloaddends have been classified according to their mode of cycloaddition to the unsaturated propellane tricyclo[5.3.1.0]undeca-2,4,9-triene (**1**). Tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) both add in a novel [6 + 2] manner to **1** and are therefore grouped together as type I cycloaddends. Singlet oxygen, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), and diethyl azodicarboxylate all add in a normal Diels–Alder [4 + 2] fashion to the seven-membered ring diene and belong to the type II class. Chlorosulfonyl isocyanate (CSI) and dichloroketene both add in a [2 + 2] mode to the cyclopentene double bond and represent type III cycloaddends. This empirical classification system could prove valuable in predicting the outcome of new cycloadditions in other systems. PTAD, for example, is better than TCNE as a model for singlet oxygen addition. Explanations for the observed differences in periselectivity are formulated with the aid of a photoelectron spectrum and geometry calculation for **1** and ab initio STO-3G calculations on a model system.

For many years, cycloaddition reactions have figured prominently in both synthetic and mechanistic organic chemistry.[2] Current understanding of the underlying principles in this area has grown from a fruitful interplay between theory and experiment and, although already highly developed,[3] continues to evolve as new experimental findings come to light. In this context, we wish to report the unexpected observation that propellane **1** (tricyclo[5.3.1.0]undeca-2,4,9-triene)[4] combines with common, electron-deficient $_\pi2$-cycloaddends in three distinct ways, i.e., [6 + 2], [4 + 2], and [2 + 2], depending on the particular partner (Scheme I). Few compounds other than fulvenes and fulvalenes participate in such varied cycloadditions.[5]

Scheme I



Grouping $_\pi2$-cycloaddends according to their mode of cycloaddition with **1** represents a classification scheme that could prove valuable in predicting the outcome of new cycloadditions in other systems (Chart I). For example, we find that 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **5**) is a good model for singlet oxygen addition to **1**, whereas tetracyanoethylene (TCNE, **3**) is not. Such similarities and differences have occasionally been reported in the past; however, systematic studies remain scarce.[6] Our work,

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[3] See, for example: Houk, K. N. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, Chapter 4.

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