

removed by running a Sephadex G-50 (Pharmacia) exclusion column. The purified protein was stored in liquid N<sub>2</sub> after dropwise addition to liquid N<sub>2</sub>. The yield of isoelectrically pure hybrid from subunits was always greater than 80%. An equivalent procedure yields the Mn hybrid in excellent yield.

The <sup>13</sup>CO hybrids were prepared by oxidizing the CO hybrid to the met hybrid by ferricyanide oxidation (4 equiv K<sub>3</sub>Fe(CN)<sub>6</sub> per heme, stirring at room temperature until oxidation was complete). The met hybrid was then desalted on a Biorad P-2 column (equilibrated with 20 mM phosphate, pH 6.6) to remove excess ferricyanide and ferrocyanide. <sup>13</sup>CO and dithionite were added quickly until the met bands disappeared and only CO bands were present in the visible spectra. The <sup>13</sup>CO hybrid was then quickly desalted by using a P-2 column as above. The samples were then exchanged with 15% D<sub>2</sub>O, 20 mM phosphate, and pH 6.6 buffer and concentrated by using an Amicon Minicon macrosolute concentrator.

The oxy hybrids were prepared as above except that air and sodium ascorbate were used instead of <sup>13</sup>CO and dithionite.

## Methods

The stopped-flow data were obtained on a Durrum stopped-flow spectrophotometer Model D-110 by mixing equal volumes of 0.4 mM heme  $\alpha$ -Zn<sub>2</sub>- $\beta$ -(FeCO)<sub>2</sub> and CO-saturated K<sub>3</sub>Fe(CN)<sub>6</sub><sup>3-</sup> (5–50 mM). Both species were in pH 6.6, 20 mM BIS-TRIS buffer. The rate of oxidation was determined by monitoring the increase in absorbance of the met band at 630 nm. Spectra were checked on a Cary 118 spectrophotometer to ensure that met formation was complete.

The ENDOR spectra were obtained at 2 K by using the instrument previously described.<sup>18</sup>

Circular dichroism spectra were recorded on a JASCO J-40 automatic recording spectropolarimeter, interfaced with a Digital PDP 11/23 com-

puter which enabled both instrumental control and signal averaging. The instrument was calibrated for each run by using camphor-*d*<sub>10</sub>-sulfonic acid as a standard. Molar ellipticities were calculated based on absorbance measurements of the hemoglobin samples. Spectra were drawn on a Tektronix 4662 interactive digital plotter after the base line was subtracted on a Tektronix 4051 graphics system. Samples were typically 15  $\mu$ M tetramer solutions, pH 7.1, 100 mM BIS-TRIS. Generally, three separate spectra were computer-averaged.

Nuclear magnetic resonance spectra were obtained with a WH-400 MHz Bruker FT-NMR spectrometer equipped with an Aspect 200 computer system. Homonuclear decoupling of the residual HDO peak was accomplished with a WEFT pulse sequence. Typical spectra widths were 6–8 KHz; 16K data points were used. Either 2,2-dimethyl 2-silapentane-5-sulfonate (DSS) or HDO were used as references for proton chemical shifts; downfield chemical shifts were assigned positive values.

Studies involving ring-current shifted resonances were undertaken by exchanging the hemoglobin hybrids with D<sub>2</sub>O, pD 7.1, 10 mM BIS-TRIS buffer. The samples were greater than 95% D<sub>2</sub>O-enriched. For such studies, relaxation delays of zero were satisfactory and flip angle values of 21° optimized spectral resolution. Typically, 2000 scans were collected.

Studies involving exchangeable proton resonances were undertaken by using a DASWEFT pulse sequence.<sup>71</sup> The samples were run in pD 7.1, 10 mM BIS-TRIS buffer, enriched to 10% D<sub>2</sub>O. All NMR spectra were collected at 24 °C, unless otherwise noted. For the CO hybrids, the 5 mM NMR tubes were capped by rubber septa and were purged with CO for 25–30 min prior to spectrum collection. Typically, 3000 scans were collected.

The <sup>13</sup>CO samples were prepared as noted above. The samples were run in pH 6.6, 20 mM phosphate, enriched to 15% D<sub>2</sub>O. Thus, no decoupling of solvent was required. Typically, 600 scans were collected.

# The Stability of Alkyl Radicals

Wing Tsang

Contribution from the Chemical Kinetics Division, National Bureau of Standards, Washington, DC 20234. Received October 19, 1984

**Abstract:** All the data on the decomposition of simple alkyl radicals have been reviewed. Together with results on the reverse addition reactions, alkyl radical combination rates, and the entropies of the alkyl radicals, the data lead to  $\Delta H_f(n\text{-C}_3\text{H}_7\cdot) = 100.5 \pm 2.1$  kJ/mol,  $\Delta H_f(i\text{-C}_3\text{H}_7\cdot) = 93.3 \pm 2.5$  kJ/mol,  $\Delta H_f(sec\text{-C}_4\text{H}_9\cdot) = 71.0 \pm 1.6$  kJ/mol,  $\Delta H_f(t\text{-C}_4\text{H}_9\cdot) = 51.7 \pm 2.2$  kJ/mol (zero barriers for CH<sub>3</sub> rotors) and  $46.2 \pm 2.2$  (10 kJ barrier for CH<sub>3</sub> rotors), and  $\Delta H_f(t\text{-C}_5\text{H}_{11}\cdot) = 32.6 \pm 4$  kJ/mol. These values are fully consistent with determinations based on the decomposition of aliphatic compounds and combination of radicals and lead to  $D(n\text{-C}_3\text{H}_7\text{-H}) = 422.5$  kJ,  $D(i\text{-C}_3\text{H}_7\text{-H}) = 415.3$  kJ,  $D(sec\text{-C}_4\text{H}_9\text{-H}) = 414.2$  kJ,  $D(t\text{-C}_4\text{H}_9\text{-H}) = 404.6$  (zero barrier), and  $D(t\text{-C}_5\text{H}_{11}\text{-H}) = 402.5$  kJ. They are all significantly higher than those generally used values recommended in a recent review but are in accord with values we suggested several years ago. It appears that previous rejection of measured alkyl radical decomposition rates is due to the general acceptance of the earlier bond energies. The rate expressions for alkyl radical decomposition which satisfy the new thermochemistry and detailed balance over the temperature range 300–800 K are the following:  $k(n\text{-C}_3\text{H}_7\cdot \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot) = 10^{13.1} \exp(-15300/T)/s$ ,  $k(i\text{-C}_3\text{H}_7\cdot \rightarrow \text{C}_3\text{H}_6 + \text{H}\cdot) = 10^{13.34} \exp(-18700/T)/s$ ,  $k(sec\text{-C}_4\text{H}_9\cdot \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\cdot) = 10^{12.97} \exp(-14700/T)/s$ ,  $k(sec\text{-C}_4\text{H}_9\cdot \rightarrow \text{C}_4\text{H}_8-1 + \text{H}\cdot) = 10^{13.11} \exp(-18300/T)/s$ ,  $k(sec\text{-C}_4\text{H}_9\cdot \rightarrow \text{c-C}_4\text{H}_8-2 + \text{H}\cdot) = 10^{12.62} \exp(-17500/T)/s$ ,  $k(sec\text{-C}_4\text{H}_9\cdot \rightarrow t\text{-C}_4\text{H}_8-2 + \text{H}\cdot) = 10^{12.66} \exp(-17100/T)/s$ ,  $k(t\text{-C}_4\text{H}_9\cdot \rightarrow i\text{-C}_4\text{H}_8 + \text{H}\cdot) = 10^{13.92} \exp(-18900/T)/s$ ,  $k(t\text{-C}_5\text{H}_{11}\cdot \rightarrow i\text{-C}_4\text{H}_8 + \text{CH}_3\cdot) = 10^{13.03} \exp(-15000/T)/s$ . Some consequences of the new bond energies with respect to our understanding of hydrocarbon free radical chemistry and the diradical mechanism for the decomposition of small ring compounds are discussed.

This paper is concerned with the thermodynamic and kinetic stability of a number of simple alkyl radicals. It is centered about the heats of formation of these radicals and represents a continuation of investigations begun several years ago.<sup>1</sup> In that work we demonstrated that the experimental data on the kinetics of the decomposition of the simple alkanes (butane, 2,3-dimethylbutane, and 2,2,3,3-tetramethylbutane) and the reverse radical combination processes are incompatible with the generally used<sup>2</sup>

heats of formation of ethyl, isopropyl, and *tert*-butyl radicals. Instead, values for  $\Delta H_f$  of the order of 10–20 kJ/mol higher were required. This has aroused a certain degree of controversy. In the case of ethyl, Hase<sup>3</sup> has demonstrated that a value for  $\Delta H_f(\text{C}_2\text{H}_5\cdot)$  of 118 kJ/mol (298 K) is derivable from the kinetics of the process  $\text{C}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}$ . There has been a considerable amount of experimental work on *tert*-butyl radicals.<sup>4,6</sup> This has

(3) W. Hase and H. Schlegel, *J. Phys. Chem.*, **86**, 3901 (1982).

(4) C. E. Canosa and R. M. Marshall, *Int. J. Chem. Kinet.*, **13**, 295 (1981).

(5) (a) M. J. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, **11**, 969 (1979).

(b) M. J. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, **15**, 1283 (1983). (c) T. S. A. Islam and S. W. Benson, *Int. J. Chem. Kinet.*, **16**, 995 (1984).

(1) W. Tsang, *Int. J. Chem. Kinet.*, **10**, 821 (1978).

(2) S. W. Benson, "Thermochemical Kinetics", John Wiley and Sons, New York, 1976.

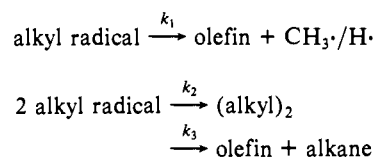
resulted in an increase of the heat of formation from the original 28 kJ/mol<sup>7</sup> to 46 kJ/mol<sup>4</sup> which approaches the value of 53 kJ/mol (298 K) recommended by us. Nevertheless, after a careful review of existing data, McMillen and Golden<sup>8</sup> continue to recommend values at 298 K of  $\Delta H_f(\text{C}_2\text{H}_5\cdot) = 108$  kJ/mol,  $\Delta H_f(\text{iso-C}_3\text{H}_7\cdot) = 76$  kJ/mol, and  $\Delta H_f(\text{t-C}_4\text{H}_9\cdot) = 36.4$  kJ/mol. Except for *tert*-butyl radicals, these are based on the original results derived from iodination experiments.<sup>9</sup> From the same source, they recommend  $\Delta H_f(\text{n-C}_3\text{H}_7\cdot) = 87.9$  kJ/mol and  $\Delta H_f(\text{sec-C}_4\text{H}_9\cdot) = 54.4$  kJ/mol. These lead to  $D(\text{primary C-H}) = 410$  kJ and  $D(\text{secondary C-H}) = 399$  kJ (where  $D(\cdot)$  refers to the enthalpy of reaction at 298 K). Such a conservative approach may be justified in view of the past lamentable history of bond dissociation energy determinations from all except metathesis processes and amply documented by Benson and O'Neal.<sup>9</sup> However, in view of the introduction of new measurement methodologies and better understanding of radical structure and unimolecular processes during the past 20 years, we believe that a fresh look at the consequences on the bond dissociation energies of simple alkanes is warranted.

This work is focussed on the rate constants for the decomposition of isopropyl, *n*-propyl, *sec*-butyl, and *tert*-butyl radicals. These results have long been regarded as suspect.<sup>9-11</sup> Reviewers have found rates and rate expressions to be incompatible with those of the better established reverse reaction (radical addition to olefin) and the generally used thermodynamics for the processes. It is the purpose of this paper to demonstrate that the higher values of the heat of formation of the alkyl radicals that we have recommended earlier on the basis of alkane decomposition data<sup>1</sup> will quantitatively resolve the discrepancies concerning the rate constants of decomposition processes involving not only isopropyl and *tert*-butyl but also *n*-propyl and *sec*-butyl radical systems. In the following, we will begin by considering the rate and thermodynamic data. Past work in this area has suffered from the limited data base considered and uncertain assumptions regarding the proper vibrational frequency assignments for the radicals. The present analysis will be carried out with the entire base and with no assumptions on frequency assignments except as dictated by experiments. From such an analysis  $\Delta G$  and  $\Delta S$  will be determined. This will lead to the heat of reaction of the following process: radical  $\rightleftharpoons$  olefin + CH<sub>3</sub>/H, from the relation  $\Delta H = T\Delta S + \Delta G$  at temperature  $T$ . Since the heats of formation of the molecules and H or CH<sub>3</sub> are known,  $\Delta H_f$  for the radical can be calculated at the reaction temperature. This is then adjusted in the standard manner to  $\Delta H_f(298)$ . We will then place these numbers in the context of other data, derive rate expressions for alkyl radical decomposition, and consider some general implications of these results.

#### Data Base

The information used to derive the heats of formation of the four radicals is summarized in Table I. In the first column of Table I is information on the decomposition of these radicals. These include all existing measurements on these systems except the original work of Bywater and Steacie.<sup>27</sup> This involved Hg-sensitized decompositions and has been repeated by other workers. These subsequent investigations are included in our tabulation. The experimental procedures used in deriving these expressions are straightforward. In all cases photochemical or chemical

sensitization is employed to generate the radical of interest. At a sufficiently high temperature, decomposition products of the radical begin to appear. At the same time the combination product is observed. The specific processes of interest are



The disproportionation process represents a complicating feature in isopropyl and *tert*-butyl radical decomposition. Fortunately, correction is straightforward since  $k_3$  has no temperature dependence and thus can be determined at sufficiently low temperatures where radical decomposition does not occur. In addition as one goes to higher temperature, recombination and disproportionation become much slower than decomposition, thus contributions from the latter to the yield of olefins become insignificant. For our purposes,  $k_1/k_2^{1/2} = (\text{rate of olefin production})/(\text{rate of dialkyl production})^{1/2}$ , and multiplication of the latter by the square root of the combination rate constant will yield the decomposition rate constant. Note that  $k_2$  is defined by the relation  $d(\text{alkyl})_2/dt = k_2(\text{alkyl})^2$ . The considerable scatter of the data is indicative of the unreliability of the rate parameters. It is probably due to the assumptions used in analyzing the data. These include (a) oversimplification of the reaction mechanism, since the desired products can arise from other sources and it is thus necessary in some cases to subtract such contributions, and (b) the assumption in some cases of a linear rate of product formation. Thus, instead of trying to fit all the experimental points or to use the rate expressions reported, we have based our treatment on the data near the midpoint of the temperature range covered in the decomposition studies.

Also included at the beginning of Table I are summaries of the available rate data for radical combination and radical addition to olefins. For *n*-propyl, we use the results of Adachi and Basco<sup>12</sup> and, as with the case of ethyl,<sup>13</sup> assume that there is no temperature dependence. In the case of isopropyl, we average the room-temperature results of Adachi and Basco<sup>12</sup> and Parkes and Quinn<sup>13</sup> and assume the temperature dependence of the latter. For *sec*-butyl, we assume that the rate expression is the same as that for isopropyl. Finally, for *tert*-butyl, we use the rate expression derived by Parkes and Quinn.<sup>13</sup> The radical addition rate parameters are taken from the review of Kerr and Parsonage<sup>18</sup> for the addition of methyl to ethylene and propylene and from Harris and Pitts<sup>14</sup> for H addition to propylene and isobutene. The former is based on the results of many studies and includes data at pressures up to 4 atm. The latter are from resonance fluorescence measurements at pressures of 50 and 100 torr of Ar and from the absence of pressure effects appear to be at or very close to the high-pressure limit.

(6) A. L. Castelhana, P. R. Marriot, and D. Griller, *J. Am. Chem. Soc.*, **103**, 4262 (1981).

(7) H. Teranishi and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2887 (1963).

(8) D. F. McMillen and D. M. Golden, "Hydrocarbon Bond Dissociation Energies" in "Annual Reviews of Physical Chemistry", B. S. Rabinovitch, Ed.; Annual Reviews Inc., Palo Alto, CA, p 493, 1982.

(9) (a) H. E. O'Neal and S. W. Benson In "Free Radicals", Vol. 2, J. K. Kochi, Ed.; Wiley, New York, 1973, p 272. (b) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, U. S. Government Printing Office, Washington, DC, 1970.

(10) J. A. Kerr and M. J. Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds", Butterworths, London, 1972.

(11) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(12) H. Adachi and N. Basco, *Int. J. Chem. Kinet.*, **13**, 367 (1981).

(13) D. Parkes and C. P. Quinn, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1953 (1976).

(14) G. W. Harris and J. N. Pitts, *J. Chem. Phys.*, **77**, 3995 (1982).

(15) J. A. Kerr and A. F. Trotman-Dickinson, *Trans. Faraday Soc.*, **55**, 572 (1959).

(16) J. G. Calvert and W. C. Sleppy, *J. Am. Chem. Soc.*, **80**, 1544 (1958).

(17) J. A. Kerr and J. Calvert, *J. Am. Chem. Soc.*, **83**, 3391 (1961).

(18) M. C. Lin and K. L. Laidler, *Can. J. Chem.*, **44**, 2927 (1966).

(19) M. M. Pappic and K. J. Laidler, *Can. J. Chem.*, **49**, 549 (1971).

(20) R. A. Back and S. Takamuku, *J. Am. Chem. Soc.*, **86**, 2558 (1961).

(21) P. Camilleri, R. M. Marshall, and H. Purnell, *Trans. Faraday Soc. I*, **71**, 1491 (1975).

(22) C. A. Heller and A. S. Gordon, *J. Am. Chem. Soc.*, **80**, 709 (1958).

(23) J. A. Kerr and A. F. Trotman-Dickinson, *Trans. Faraday Soc.*, **55**, 922 (1959).

(24) M. C. Lin and K. J. Laidler, *Can. J. Chem.*, **45**, 1315 (1967).

(25) J. G. Calvert, *Chem. Rev.*, **59**, 569 (1959).

(26) R. N. Birrell and A. F. Trotman Dickinsen, *J. Chem. Soc.*, 4218 (1960).

(27) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 172 (1951).

**Table I.** Summary of Experimental and Calculated Results for the Processes  $R \cdot \rightleftharpoons \text{olefin} + \text{CH}_3/\text{H} \cdot$  with  $k(\text{combination})$  and  $k(\text{addition})$  as Follows

	$k(2 n\text{-propyl} \rightarrow n\text{-hexane}) = 10^{10} \text{ L}/(\text{mol}\cdot\text{s})$	(ref 12)
	$k(2 \text{isopropyl} \rightarrow 2,3\text{-dimethylbutane}) = 6 \times 10^9 (300/T)^{1/2} \text{ L}/(\text{mol}\cdot\text{s})$	(ref 12, 13)
	$k(2 \text{sec-butyl} \rightarrow 3,4\text{-dimethylhexane}) = 6 \times 10^9 (300/T)^{1/2} \text{ L}/(\text{mol}\cdot\text{s})^a$	
	$k(2 \text{tert-butyl} \rightarrow 2,2,3,3\text{-tetramethylbutane}) = 2.4 \times 10^9 (300/T)^{3/2} \text{ L}/(\text{mol}\cdot\text{s})$	(ref 13)
	$k(\text{CH}_3 \cdot + \text{C}_2\text{H}_4 \rightarrow n\text{-C}_3\text{H}_7 \cdot) = 3.3 \times 10^8 \exp(-3877/T) \text{ L}/(\text{mol}\cdot\text{s})$	(ref 10)
	$k(\text{H} \cdot + \text{C}_3\text{H}_6 \rightarrow i\text{-C}_3\text{H}_7 \cdot) = 6.1 \times 10^9 \exp(-609/T) \text{ L}/(\text{mol}\cdot\text{s})$	(ref 14)
	$k(\text{CH}_3 \cdot + \text{C}_3\text{H}_6 \rightarrow \text{sec-C}_4\text{H}_9 \cdot) = 1.66 \times 10^8 \exp(-3726/T) \text{ L}/(\text{mol}\cdot\text{s})$	(ref 10)
	$k(\text{H} \cdot + i\text{-C}_4\text{H}_8 \rightarrow t\text{-C}_4\text{H}_9 \cdot) = 3.7 \times 10^{10} \exp(-849.5/T) \text{ L}/(\text{mol}\cdot\text{s})$	(ref 14)
	<hr/>	
	decomposition rates	equilibrium properties
Method (ref)	$\log K_p(\text{reaction, atm})$	$\Delta H_f(R \cdot)$ at 300 K
$k(\text{dec})/k^{1/2}(\text{comb}) (\text{L}\cdot\text{s}/\text{mol})^{1/2}$ at	$\log K_f(\text{radical})$	BDE (RH $\rightarrow$ R $\cdot$ + H $\cdot$ )
$T$ (K) and $P$ (torr)	at $T$	(kJ/mol)
$k/k_\infty$ (dev from high pressure)		
I. $n\text{-C}_3\text{H}_7 \rightarrow \text{CH}_3 \cdot + \text{C}_2\text{H}_5 \cdot$ ; R $\cdot$ = $n\text{-C}_3\text{H}_7$		
1. photolysis of $n$ -butyraldehyde (15)		
$10^{6.2} \exp(-12698/T)$ at	-1.93	100.6
543-694 K and 20 torr	-18.94	422.4
$k/k_\infty \sim 0.83$ (600 K, 20 torr)	at 600 K	
$k(\text{dec}, \infty) = 122/\text{s}$ at 600 K		
2. azomethane-sensitized dec of $n$ -butyraldehyde (16)	-3.24	105
$10^{10.57} \exp(-17573/T)$ at	-20.89	426.8
471-549 K and 100 torr	at 500 K	
$k/k_\infty \sim 1$ (500 K, 100 torr)		
$k(\text{dec}, \infty) = 2.04/\text{s}$ at 500 K		
3. photolysis of azopropane (17)	-3.71	100
$10^{9.86} \exp(-17372/T)$ at	-20.42	421.8
$k/k_\infty \sim 0.88$ (500 K, 13 torr)		
$k(\text{dec}, \infty) = 0.67/\text{s}$ at 500 K		
4. azomethane-sensitized dec of propane (18)	-2.92	100
$10^{8.37} \exp(-15810/T)$ at	-19.43	421.8
533-573 K and 55-195 torr	at 550 K	
$k/k_\infty \sim 1$ (550 K, 195 torr)		
$k(\text{dec}, \infty) = 7.7/\text{s}$ at 550 K		
5. Hg-sensitized dec of propane (19)	-1.70	103.3
$10^{9.2} \exp(-16415/T)$ at	-19.18	425.1
525-623 K and 5-700 torr	at 600 K	
$k/k_\infty \sim 1$ (600 K, 700 torr)		
$k(\text{dec}, \infty) = 210/\text{s}$ (600 K)		
6. Hg-sensitized dec of propane (20)	-1.84	101.9
$10^{6.33} \exp(-12638/T)$ (b) at	-19.05	423.7
573-673 K	at 600 K	
$k/k_\infty \sim 1$ (600 K, 300 torr)		
$k(\text{dec}, \infty) = 153/\text{s}$ at 600 K		
7. azomethane-sensitized dec of propane (21)	-0.79	90.0
$10^{7.8} \exp(-16367/T)$ at	-16.90	411.8
676-813 K and 10-26 torr	at 750 K	
$k/k_\infty \sim 0.42$ (750 K, 15 torr)		
$k(\text{dec}, \infty) = 5000/\text{s}$ at 750 K		
II. $i\text{-C}_3\text{H}_7 \cdot \rightarrow \text{C}_3\text{H}_6 + \text{H} \cdot$ ; R $\cdot$ = $i\text{-C}_3\text{H}_7$		
1. photolysis of diisopropyl- $d_2$ ketone (22)	-5.74	93.7
$10^{7.53} \exp(-17623/T)$ (c) at	-17.41	415.6
673-773 K at 15 torr	at 700 K	
$k/k_\infty \sim 0.6$ (700 K, 15 torr)		
$k(\text{dec}, \infty) = 41.4$ at 700 K		
2. photolysis of isobutyraldehyde (23)	-5.67	93.2
$10^{8.3} \exp(-18580/T)$ at	-17.38	415.1
673-773 K at 30 torr	at 700 K	
$k/k_\infty \sim 0.7$ (700 K, 30 torr)		
$k(\text{dec}, \infty) = 53.3/\text{s}$ at 700 K		
3. Hg-sensitized dec of propane (19)	-7.50	94.8
$10^{9.1} \exp(-19486/T)$ at	-18.48	416.7
523-623 K and 5-700 torr	at 600 K	
$k/k_\infty \sim 1$ (600 K, 700 torr)		
$k(\text{dec}, \infty) = 0.65/\text{s}$ at 600 K		
4. Hg sensitized decomposition of propane (20)	-7.52	94.6
$10^{8.5} \exp(-18630/T)$ at	-18.46	416.5
573-673 K and 300 torr	at 600 K	
$k/k_\infty \rightarrow 1$ (600 K, 300 torr)		
$k(\text{dec}, \infty) = 0.52/\text{s}$ at 600 K		

Table I (Continued)

decomposition rates		equilibrium properties	
5. azomethane-sensitized dec of propane (21)		-5.14	92.3
10 <sup>9.1</sup> exp(-20579/T) at		-16.90	414.2
678-813 K and 10-26 torr		at 750 K	
$k/k_{\infty} \sim 0.5$ (750 K, 15 torr)			
$k(\text{dec}, \infty) = 189/\text{s}$ at 750 K			
III. $\text{sec-C}_4\text{H}_9 \cdot \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3 \cdot$ ; R = $\text{sec-C}_4\text{H}_9 \cdot$			
1. photolysis of 2-methylbutanal (24)		-2.30	72.0
10 <sup>8.66</sup> exp(-15407/T) (d) at		-21.74	416.3
520-660 K and 50 torr		at 550 K	
$k/k_{\infty} \sim 1$ (550 K, 50 torr)			
$k(\text{dec}, \infty) = 21/\text{s}$ at 550			
2. azomethane-sensitized dec of butane (25)		-1.87	68.6
10 <sup>9.62</sup> exp(-16415/T) at		-20.98	412.9
533-613 K and 60-200 torr		at 600 K	
$k/k_{\infty} \sim 1$ (600 K, 200 torr)			
$k(\text{dec}, \infty) = 358/\text{s}$ at 600 K			
IV. $t\text{-C}_4\text{H}_9 \cdot \rightarrow \text{C}_4\text{H}_8 + \text{H} \cdot$ ; R = $t\text{-C}_4\text{H}_9 \cdot$			
1. photolysis of pivaldehyde (26)		-5.64	47.0
10 <sup>10.8</sup> exp(-21953/T) at		-19.67	399.8
663-800 K and 40 torr		at 750 K	(zero barrier)
$k(\text{dec}, \infty) = 432.6/\text{s}$ at 750 K			42.3
			395.1
			(10 kJ barrier for Me rotors)
2. azomethane-sensitized dec of isobutane (4)		-7.95	53.1
0.9 × 10 <sup>-6</sup> at 584 K		-20.61	405.8
1.59 × 10 <sup>-6</sup> at 594 K		at 600 K	(zero barrier)
2.87 × 10 <sup>-6</sup> at 604 K			for Me rotors)
and 53-272 torr			48.1
$k/k_{\infty} \sim 1$ at 600 K and 272 torr			400.8
$k(\text{dec}, \infty) = 2.04/\text{s}$ at 600 K			(10 kJ barrier for Me rotors)

<sup>a</sup> Assumed to be equal to  $k(\text{isopropyl} \rightarrow 2,3\text{-dimethylbutane})$ . <sup>b</sup> Corrected with  $n$ -propyl/isopropyl from ref 19. <sup>c</sup> Corrected to reflect rates of production given in the table of ref 22. <sup>d</sup> Results based on units in figures and tables of ref 24.

Table II. Alkyl Radical Entropies (J/mol·K)

temp (K)	$n\text{-C}_3\text{H}_7 \cdot^a$	$i\text{-C}_3\text{H}_7 \cdot^b$	$\text{sec-C}_4\text{H}_9 \cdot^c$	$t\text{-C}_4\text{H}_9 \cdot(0)^d$	$t\text{-C}_4\text{H}_9 \cdot(2400)^e$	$t\text{-C}_5\text{H}_{11} \cdot^f$
300	289.41	289.70	336.69	320.10	309.41	367.43
500	334.05	331.66	392.58	370.86	365.93	432.08
700	374.22	369.82	444.05	419.33	416.44	493.61
900	409.91	404.43	490.36	464.09	462.21	550.04
1100	441.83	435.67	532.0	504.99	503.80	601.24
1300	470.45	464.04	569.59	542.24	541.40	647.71
1500	496.43	489.84	603.71	576.19	575.50	689.96

<sup>a</sup> Frequencies (degeneracy) 3100 (2), 2960 (5), 1440 (5), 1390 (1), 1100 (1), 990 (4), 980 (1), 960 (1), 530 (1), 330 (1); 1 hindered rotor with barrier, 15 kJ, and  $I_{40} = 4.2 \times 10^{-40}$  g·cm<sup>2</sup> with symmetry 3 and 1 free rotor with  $I = 2.7 \times 10^{-4}$  g·cm<sup>2</sup> and symmetry 2. Moment of inertia,  $2.54 \times 10^{-115}$  g·cm<sup>2</sup>; symmetry, 1; ground-state degeneracy, 2. References 28 and 29. <sup>b</sup> Frequencies (degeneracy) 3100 (1), 2960 (6), 1440 (6), 1300 (1), 1200 (1), 990 (4), 950 (1), 397 (1), 367 (1); 2 free rotors,  $I = 4.2 \times 10^{-40}$  g·cm<sup>2</sup> and symmetry 3. Moment of inertia,  $2.67 \times 10^{-115}$  g·cm<sup>2</sup>; symmetry, 2; ground-state degeneracy, 2. References 29 and 30. <sup>c</sup> Frequencies (degeneracy) 3100 (1), 2960 (8), 1440 (8), 1300 (1), 1200 (1), 990 (6), 960 (1), 950 (1), 398 (1), 367 (1), 350 (1); 1 hindered rotor with 15 kJ barrier,  $I = 4.8 \times 10^{-40}$  g·cm<sup>2</sup>, and symmetry 3 and 2 free rotors with  $I = 1.4 \times 10^{-39}$  and  $4.8 \times 10^{-40}$  g·cm<sup>2</sup> and symmetry 1 and 3. Moment of inertia,  $1.22 \times 10^{-114}$  g·cm<sup>2</sup>; symmetry, 1; ground-state degeneracy, 2. Estimates based on ref 29, 30, and 32. <sup>d,e</sup> Frequencies (degeneracy) 2931 (6), 2825 (3), 1455 (6), 1370 (3), 1279 (1), 1252 (2), 1189 (2), 1126 (1), 992 (2), 733 (1), 541 (2), 200 (1); 3 free rotor (0)  $I = 4.7 \times 10^{-40}$  g·cm<sup>2</sup> symmetry 3, or 3 hindered rotor (2400)  $I = 4.7 \times 10^{-40}$  g·cm<sup>2</sup>, symmetry 3 and 10 kJ barrier to internal rotation. Moment of inertia,  $2.24 \times 10^{-114}$  g·cm<sup>2</sup>; symmetry, 3; ground-state degeneracy, 2. Reference 31. <sup>f</sup> Frequencies (degeneracy) 2931 (9), 2825 (2), 1455 (8), 1370 (3), 1279 (1), 1252 (2), 1189 (2), 1126 (1), 992 (3), 990 (2), 733 (1), 541 (2), 380 (1), 200 (1); 1 hindered rotor with  $I = 4.8 \times 10^{-40}$  g·cm<sup>2</sup> symmetry = 3 and barrier 15 kJ; 3 free rotors with  $I = 4.8 \times 10^{-40}$  g·cm<sup>2</sup>,  $4.8 \times 10^{-40}$ , and  $2.1 \times 10^{-39}$ , symmetry 3, 3, and 1. Moments of inertia,  $8.59 \times 10^{-114}$  g·cm<sup>2</sup>; symmetry, 1; ground-state degeneracy, 2. Estimates based on ref 30 and 32.

Entropies of the alkyl radicals as a function of temperature can be found in Table II. These are based principally on the studies of Pacansky and co-workers.<sup>28,30,31</sup> They have directly observed in low-temperature matrices the infrared spectra of alkyl radicals and verified and extended these observations through theoretical calculations. It is interesting to note that the calculated entropies of  $n$ -propyl and ethyl are in exact agreement with those derived by Purnell and Quinn<sup>29</sup> on the basis of an assumed structure and vibrational frequencies published 20 years ago. In the case of  $\text{sec}$ -butyl and  $\text{tert}$ -amyl radicals we have made use of a similar

procedure and where applicable used the frequency assignments from the normal alkanes.<sup>32</sup> Thus except for  $\text{tert}$ -butyl radicals it would appear that the entropies of alkyl radicals are known to the same accuracy as those of the normal alkanes. For  $\text{tert}$ -butyl radicals, there is a question regarding the height of the barrier to rotation of the methyl rotors. These range from zero to 10 kJ. Although we believe the data favor the former value, we have carried out entropy calculations for the two extremes in order to bracket all possibilities.

Combination of the entropy data and the  $A$  factors of radical addition to olefins permit us to calculate  $A$  factors for radical decomposition, using the relation  $A(\text{dec})/A(\text{addition}) = \exp(\Delta S/R)/eRT$  (where  $R$  is the gas constant and is equal to 8.31

(28) J. Pacansky, D. E. Horne, G. P. Gardini, and J. Bargon, *J. Phys. Chem.*, **81**, 23 (1977).

(29) J. H. Purnell and C. P. Quinn, *J. Chem. Soc.*, 4049 (1964).

(30) J. Pacansky and H. Coufal, *J. Chem. Phys.*, **12**, 3298 (1980).

(31) J. Pacansky and J. S. Chang, *J. Chem. Phys.*, **74**, 5539 (1981).

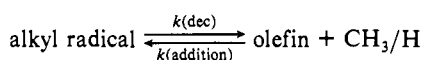
(32) K. S. Pitzer and J. E. Kilpatrick, *Chem. Rev.*, **47**, 435 (1947).

**Table III.** Rate Expressions for the Decomposition of Some Simple Alkyl Radicals

	$A_{\infty}/s$	$E_{\infty}$ (kJ)
$n\text{-C}_3\text{H}_7\cdot \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\cdot$	$10^{13.1}$	126.8
$i\text{-C}_3\text{H}_7\cdot \rightarrow \text{C}_3\text{H}_6 + \text{H}\cdot$	$10^{13.34}$	155.6
$sec\text{-C}_4\text{H}_9\cdot \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\cdot$	$10^{12.97}$	122.7
$sec\text{-C}_4\text{H}_9\cdot \rightarrow 1\text{-C}_4\text{H}_8 + \text{H}\cdot$	$10^{13.11}$	152.2
$sec\text{-C}_4\text{H}_9\cdot \rightarrow c\text{-C}_4\text{H}_8\text{-}2 + \text{H}\cdot$	$10^{12.62}$	145.2
$sec\text{-C}_4\text{H}_9\cdot \rightarrow t\text{-C}_4\text{H}_8\text{-}2 + \text{H}\cdot$	$10^{12.66}$	141.9
$t\text{-C}_4\text{H}_9\cdot \rightarrow i\text{-C}_4\text{H}_8 + \text{H}\cdot$ (zero barrier)	$10^{13.92}$	157.1
$t\text{-C}_4\text{H}_9\cdot \rightarrow i\text{-C}_4\text{H}_8 + \text{H}\cdot$ (10 kJ barrier)	$10^{14.2}$	161.0

J/K or 0.082 atm·L/mol·K). These are summarized in the second column in Table III. With these numbers it is possible to make an estimate of the extent of departures from the high-pressure limit for the rate of radical decomposition reactions on the basis of RRKM calculations.<sup>33</sup> For this purpose vibrator models have been constructed to reproduce the calculated  $A$  factors. It is well-known<sup>33</sup> that details of the frequency distribution are relatively unimportant for the present purpose as long as a correct entropy of activation is determined. For weak collisional effects a step size down of 1000 cm<sup>-1</sup> for<sup>34</sup> deactivation was used in order to determine the collisional efficiency. This is the value we have found to be appropriate for the data on ethane and ethyl radical decomposition. In any case we are very close to the high-pressure limit for all these compounds. Thus  $k/k_{\infty}$  values are not particularly sensitive to the collisional efficiency. The activation energy we use here is the final value that we derived as a result of our analysis. Thus, in practice, we derive our  $k/k_{\infty}$  value on the basis of a series of iterations. That is we begin by using the experimental rate constant (therefore assuming  $k/k_{\infty} = 1$ ) and on that basis determine heat of formation for the radical. This leads to an activation energy for the process. We then carry out a RRKM calculation, determine  $k/k_{\infty}$ , and thus obtain a new  $k_{\infty}$ . We can then proceed to the next cycle. Here again, the results are not particularly sensitive to the possible variations in activation energy due to its closeness to the high-pressure limit. On this basis,  $k/k_{\infty}$  values are listed in Table I as well as the corrected rate constants for decomposition  $k(\text{dec}, \infty)$ .

Calculated equilibrium constants  $K_p$  can be found in the second column of Tables I. They are for the reactions



and the rate constant in concentration units is derived from the relation

$$K_p(\text{atm}) = k(\text{dec})RT/k(\text{addition})$$

where as mentioned earlier  $T$  is close to the midpoint of the temperature range covered by the decomposition studies and  $R$  is the appropriate gas constant. Some extrapolation of the addition and combination rates is thus required. The H-addition reactions have been studied at temperatures up to 441 K while the CH<sub>3</sub>-addition processes have been determined up to 500 K. We have proceeded on the assumption that the addition and combination data are more reliable and therefore can be extrapolated satisfactorily to the higher temperatures where decomposition processes are occurring. If a choice must be made, preference should be given to the lowest temperature decomposition studies. These begin at about 500 K, and extrapolation errors will be a minimum. In our analysis we have weighed all data equally. The scatter is sufficiently low so that a more critical approach is unnecessary.

### Heats of Formation

The information base summarized in Table I together with the well-established equilibrium constant of formation of the olefins and that of the H· or CH<sub>3</sub>· radicals permits calculation of the heats

of formation of the four alkyl radicals through the familiar relation

$$-\Delta G = 2.303RT \log K_f = -\Delta H_f + T\Delta S \quad (\text{at temp } T)$$

where  $K_f$  is the equilibrium constant of formation of the appropriate alkyl radical. From standard formulas it is easy to compute BDE(300), defined as  $\Delta H_f(\text{H}\cdot) + \Delta H_f(\text{alkyl radical}) - \Delta H_f(\text{alkane})$  at 300 K. The results of such calculations can be found in the last column of Table I.

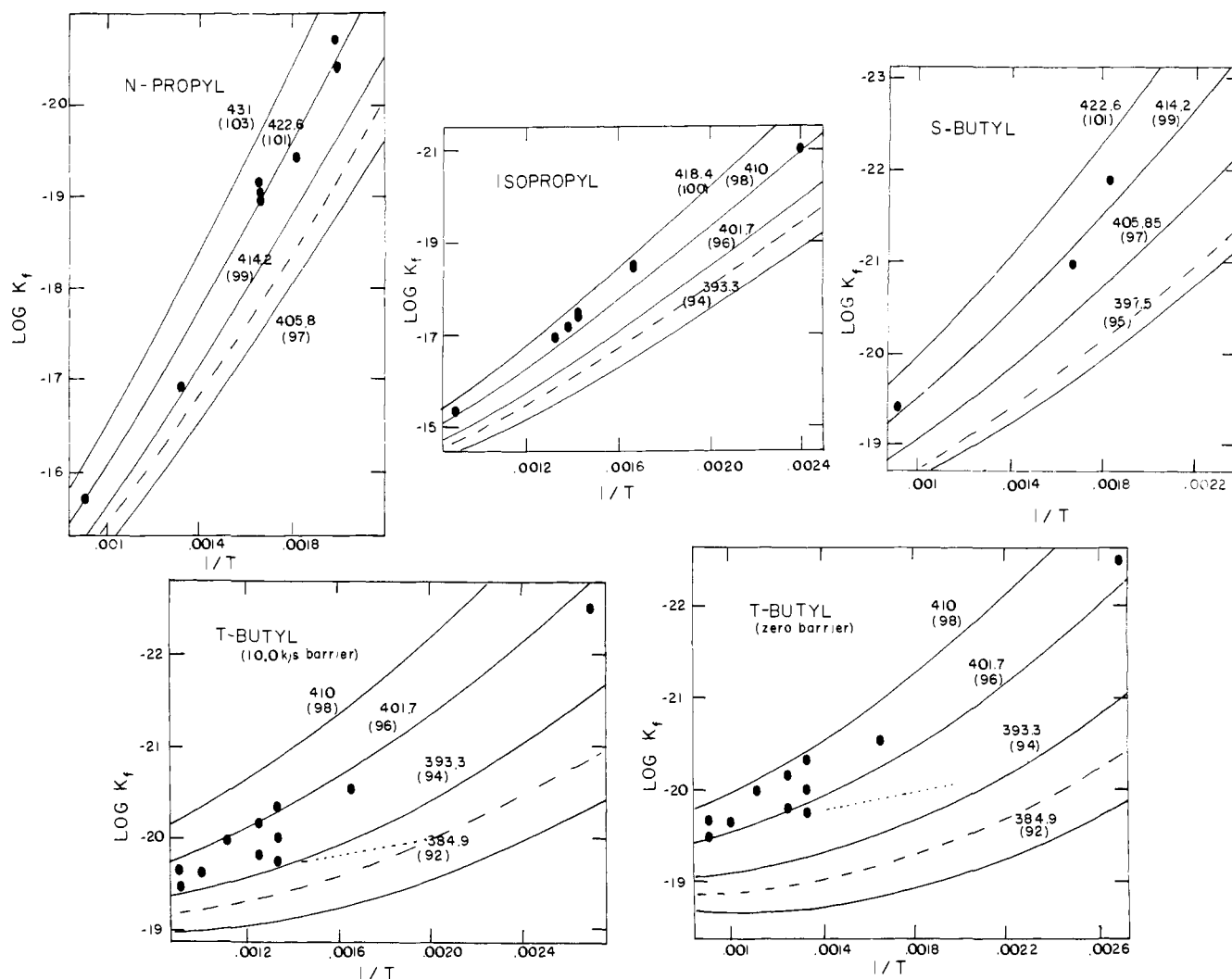
In order to put these numbers in a more general context, we have plotted in Figure 1  $\log K_f(\text{R}\cdot)$  vs.  $1/T$  for a variety of possible heats of formation of the alkyl radicals using the entropies in Table II. Superimposed on these curves are points representing the determinations from the alkyl radical decomposition process discussed above as well as results derived from the decomposition of simple alkanes and alkenes. The data on the alkanes and alkenes are summarized in Table IV. These include shock tube studies on 2,3-dimethylbutane and hexamethylethane and the radical buffer studies on isopropyl and *tert*-butyl radicals which we have discussed in an earlier paper. In addition, we have also included a wide variety of results from static and flow experiments as well as shock tube results that yield *n*-propyl and *sec*-butyl radicals. Finally, for comparison we have outlined in Figure 1 the values for  $\log K_f$  that correspond to McMillen and Golden's recommended heats of formation.

It is clear that for each radical all the data on its formation (from hydrocarbon decomposition) or its decomposition lead to a single value for its heat of formation. The variation is in the 2–3 kJ range. The data span the temperature range from 350 to 1100 K. Equilibrium properties of a few compounds have been determined over such a range. The results of the present analysis lead to  $\Delta H_f(n\text{-C}_3\text{H}_7\cdot) = 100.5 \pm 2.1$  kJ/mol,  $\Delta H_f(i\text{-C}_3\text{H}_7\cdot) = 93.3 \pm 2.5$  kJ/mol,  $\Delta H_f(sec\text{-C}_4\text{H}_9\cdot) = 71.0 \pm 1.6$  kJ/mol, and  $\Delta H_f(t\text{-C}_4\text{H}_9\cdot) = 51.7 \pm 2.2$  kJ/mol. We have taken the barrier to rotation for the methyl rotors adjacent to the radical site to be zero in all cases. If a 10-kJ barrier is assumed for *tert*-butyl, the resulting heat of formation is  $46.2 \pm 2.5$  kJ/mol. Equivalently, the bond dissociation energies are  $D(n\text{-C}_3\text{H}_7\text{-H}) = 422.5$  kJ,  $D(i\text{-C}_3\text{H}_7\text{-H}) = 415.3$  kJ,  $D(sec\text{-C}_4\text{H}_9\text{-H}) = 414.2$  kJ,  $D(t\text{-C}_4\text{H}_9\text{-H}) = 404.6$  kJ (zero barrier), and  $D(t\text{-C}_4\text{H}_9\text{-H}) = 399.1$  kJ (10 kJ barrier). These values are incompatible with the generally used numbers recommended by McMillen and Golden and derived from the iodination studies. Particularly noteworthy is the magnitude of the discrepancy in the equilibrium constants. They range from a factor of 3 to 5 at the highest temperatures (from the shock tube studies) to a factor of 10–20 in the intermediate temperature range, where alkyl radical decompositions are carried out, to a factor of 100 at the lowest temperature (radical buffer studies). Except for the production of *n*-propyl from hexene-1, the hydrocarbon decomposition studies all involve the production of two identical radicals. Thus the magnitude of the difference in terms of the logarithms of the equilibrium constants is increased by a factor of 2. In the case of hexene-1 decomposition, we have used a value for allyl heat of formation that we have previously derived.<sup>1</sup> It is approximately 10 kJ higher than the recommendations of McMillen and Golden.<sup>8</sup> It should be noted that in the analysis we have not considered the data on processes in which two different large alkyl radicals are formed, for example, 2,2,3-trimethylpentane  $\rightarrow$  *sec*-butyl + *tert*-butyl. This is because in order to carry out the calculations properly an iterative procedure must be used. Nevertheless, the existing data on such systems are fully compatible with our radical heats of formation. We also note that the data from very low pressure pyrolysis and chemical activation experiments are equally compatible with our hydrocarbon decomposition rates.<sup>1</sup> These measurements however determine only one of the two rate parameters.

Since  $K_p = k_f/k_r$ , if one accepts in all cases the correctness of the reverse rates ( $k_r$ ) then the discrepancy in heats of formation is directly reflected in the decomposition rates. On this basis it is hardly surprising that those who accept the radical heats of formation from the iodination studies should always have found earlier determinations of radical and hydrocarbon decomposition rates to be in error. What has now been demonstrated is that if

(33) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, 1972.

(34) W. Tsang, to be published.



**Figure 1.** Equilibrium constants (in units of atms) of formation for *n*-propyl, isopropyl, *sec*-butyl, *tert*-butyl (with freely rotating CH<sub>3</sub> groups), and *tert*-butyl (with barrier to internal rotation of methyl groups of 10 kJ) as a function of temperature (K<sup>-1</sup>) for various bond dissociation energies. Entropies are from Table II. Values are in kJ. Numbers in parentheses are in kcal. The long dashed line represents equilibrium constants based on recommendations of McMillen and Golden,<sup>7</sup> and the short dashed line for *tert*-butyl are calculated results based on a combination of the work of Teranishi and Benson<sup>6</sup> and Rossi and Golden.<sup>5</sup> Points are experimental values from Tables I and IV.

this is the case, for every study, they are in error in precisely the same manner! This is unlikely, and in the following we give our rationale. In the hydrocarbon decomposition studies, the measured rates are too slow in comparison to those required if McMillen and Golden's numbers are correct. Except for fall-off effects there is no mechanism for slowing the rate of an elementary gas-phase process. We have accordingly checked the neopentane decomposition results for pressure effects due to unimolecular fall-off behavior using an *A* factor of  $\sim 10^{17}$ /s (see Table IV), and it is clear that all the experimental results are substantially at the high-pressure limit. On the other hand, our alkyl radical decomposition rates are faster (see Figure 1) than that required by the older heats of formation. The possibility of alternate reaction pathways for the formation of the radical decomposition products must be considered. This is rendered unlikely by the fact that the results were obtained in experiments where widely different methods were used. For example, for *n*-propyl radical decomposition, *n*-propyl radicals were produced from the mercury-sensitized decomposition of propane,<sup>19</sup> the azomethane-sensitized pyrolysis of propane,<sup>18</sup> the photolysis of azopropane,<sup>17</sup> and the photolysis of *n*-butyraldehyde.<sup>15</sup> It would be extraordinary if a more complex mechanism in each case would produce essentially the same result. Of course the scatter in rate parameters is indicative of the possibility of complicating features. The discrepancies between present and earlier values for the heats of formation are, however, so large that this scatter is of minor consequence within the context of the present third law treatment.

A final possibility is errors in the combination rates. However, it will be noted that while lowering of the rates by a factor of 10 to 20 would bring the high temperature stable compound decomposition data into line with the older heat of formation, for the lower temperature results factors of several hundred will be required. This will lead to the implication of a barrier to recombination. In addition, the totality of all the data on radical combination, particularly considering the variety of methods, very low pressure pyrolysis, modulation spectroscopy, and flash photolysis, makes errors of this magnitude needed very unlikely. We note that the original interpretation of the radical buffer reaction<sup>9</sup> was in fact that the combination rate was slow. However, as pointed out by Griller and Ingold,<sup>46</sup> a recombination rate constant of  $3 \times 10^6$  L/mol-s for *tert*-butyl radicals is lower than the liquid phase rate.

The present results on *tert*-butyl radicals are particularly interesting because this is the radical which has aroused the greatest amount of recent interest. Of particular importance is the work of Rossi and Golden<sup>5a</sup> for the rate of reaction of the process  $t\text{-C}_4\text{H}_9 + \text{HI} \rightarrow \text{C}_4\text{H}_{10} + \text{I}$ . In combination with the original studies of Teranishi and Benson,<sup>7</sup> an equivalent determination of the equilibrium constant of formation of *tert*-butyl radical can be derived. Results for the temperature range 500–700 K can be seen in Figure 1. More recently, Rossi and Golden<sup>5b</sup> have carried out similar studies in the 300–412 K range. In addition Islam and Benson<sup>5c</sup> have determined the equilibrium constant for the reaction  $\text{Br} + i\text{-C}_4\text{H}_{10} \rightleftharpoons t\text{-C}_4\text{H}_9 + \text{HBr}$ . They conclude that

Table IV. Summary of Experimental Kinetic and Calculated Thermodynamic Results for Hydrocarbon Decomposition Processes

rate data		equilibrium properties	
reaction		$\log K_p(\text{reaction, atm})$	$\Delta H_f^\circ(\text{R}\cdot)$ at 300 K
$k(\text{dec})$ at $T$ with method (ref)		$\log K_f(\text{radical})$	BDE (RH $\rightarrow$ R $\cdot$ + H $\cdot$ )
$k(\text{comb})$ at $T$ with method (ref)		at $T$	(kJ/mol)
I. <i>n</i> -Propyl; $\text{C}_3\text{H}_5\text{-}n\text{-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_5\cdot + n\text{-C}_3\text{H}_7\cdot$			
1. $k(\text{dec}) = 10^{15.9} \exp(-35600/T)/\text{s}$ from comparative rate shock tube experiment at 1100 K (31)		-6.49 -15.65 at 1100 K based on $\log K_f(\text{allyl}) = -13.37$ $\Delta H_f^\circ(\text{allyl}, 298) = 174.5$	100.4 422.4
$k(\text{comb}) = 2 \times 10^{10}$ L/mol-s from flash photolysis studies on <i>n</i> -propyl at 300 K and allyl (300-600 K) and geometric mean rule (35, 36)			
II. Isopropyl; $(i\text{-C}_3\text{H}_7)_2 \rightarrow 2 i\text{-C}_3\text{H}_7\cdot$			
1. $k(\text{dec}) = 10^{16.3} \exp(-38300/T)$ from comparative rate shock tube results at 1100 K (37)		-6.24 -15.27 at 1100 K	89.1 410.9
$k(\text{comb}) = 10^{9.8}(300/T)^{0.5}$ see Table I			
2. $k(\text{dec}) = 10^{17.1} \exp(-39600/T)/\text{s}$ from static pyrolysis at 725 K (38)		-14.32 -17.13 at 725 K	92.5 414.4
$k(\text{comb})$ as in II.1			
3. $k(\text{dec}) = 10^{-25.37}/\text{s}$ from radical buffer study at 414 K (1)		-33.58 -20.99 at 415 K	89 410.9
$k(\text{comb})$ as in II.1			
III. <i>sec</i> -Butyl; $(\text{sec-C}_4\text{H}_9)_2 \rightarrow 2 \text{sec-C}_4\text{H}_9\cdot$			
1. $k(\text{dec}) = 10^{16.5} \exp(-37800/T)/\text{s}$ from comparative rate single pulse experiments at 1100 K (37)		-5.86 -19.43 at 1100 K	72.0 416.3
$k(\text{comb}) = k(\text{comb})$ , isopropyl			
IV. <i>tert</i> -Butyl; $(t\text{-C}_4\text{H}_9)_2 \rightarrow 2 t\text{-C}_4\text{H}_9\cdot$			
1. $k(\text{dec}) = 10^{16.4} \exp(-34400/T)/\text{s}$ from comparative rate single pulse shock tube experiments at 1100 K (37)		-3.75 -19.47 at 1100 K	49 401.8 (zero barrier, methyl rotors)
$k(\text{comb}) = 10^{9.4}(300/T)^{1.5}$ from modulation spectroscopy and VLPP (13)			42.3 395.1 (10 kJ barrier, Me rotors)
2. $k(\text{dec}) = 10^{17.4} \exp(-36000/T)/\text{s}$ from inhibited dec in flow system at 800 K (42)		-9.06 -19.79 at 800 K	49.6 402.4 (zero barrier, Me rotors)
$k(\text{comb})$ ; as given in IV.1			43.9 396.6 (10 kJ barrier, Me rotors)
3. $k(\text{dec}) = 10^{17.25} \exp(-39740/T)/\text{s}$ from static studies with O <sub>2</sub> (44) at 750 K (44)		-10.45 -19.68 at 750 K	46.9 399.6 (zero barrier, Me rotors)
$k(\text{comb})$ ; as given in IV.1			41.7 394.4 (10 kJ barrier, Me rotors)
4. $k(\text{decomp}) = 10^{-25.33}/\text{s}$ from radical buffer study at 373 K (1)		-33.08 -22.23 at 373 K	50.0 403.7 (zero barrier, Me rotors)
$k(\text{comb})$ ; as given in IV.1			45.7 399.4 (10 kJ barrier, Me rotors)
$t\text{-C}_4\text{H}_9\text{-CH}_3 \rightarrow t\text{-C}_4\text{H}_9\cdot + \text{CH}_3\cdot$			
5. $k(\text{dec}) = 10^{16.9} \exp(-40990/T)/\text{s}$ from comparative rate single pulse shock tube studies at 1100 K (37)		-6.93 -19.67 at 1100 K	53.1 406.8 (zero barrier, Me rotors)
$k(\text{comb}) = 10^{9.98}(300/T)^{1.07}$ from $t\text{-C}_4\text{H}_9\cdot$ combination rate (13) and $k(\text{comb})(2\text{CH}_3\cdot) = 10^{10.35}(300/T)^{0.64}$ L/mol-s based on survey of existing data (39)			47.3 401 (10 kJ barrier, Me rotors)
6. $k(\text{dec}) = 10^{16.9} \exp(-40530/T)/\text{s}$ from studies with wall-less reactor at 1000 K (40)		-8.50 -19.63 at 1100 K	51 404.7 (zero barrier, Me rotors)
$k(\text{comb})$ as given in IV.5			46.4 400.1 (10 kJ barrier, Me rotors)
7. $k(\text{dec}) = 10^{17.7} \exp(-42840/T)/\text{s}$ from flow studies at 900 K (41)		-10.80 -19.98	54.4 408.1 (zero barriers, Me rotors)
$k(\text{comb})$ as given in IV.5			49.4 403.1 (10 kJ barrier, Me rotors)

Table IV (Continued)

rate data	equilibrium properties	
8. $k(\text{dec}) = 10^{16.1} \exp(-39730/T)/\text{s}$ from static studies near 800 K  $k(\text{comb})$ as given in IV.5	-13.40	55.2
	-20.16	408.9
		(zero barrier, Me rotors)
		49.8 403.5
9. $k(\text{dec}) = 10^{16.8} \exp(-41300/T)/\text{s}$ from static studies at 750 K (45)  $k(\text{comb})$ as given in IV.5	-15.11	55.1
	-20.35	408.8
	at 750 K	(zero barrier, Me rotors)
		50.2 403.9
		(10 kJ barrier, Me rotors)

Table V. Calculated and Experimental Data on the Isomerization of Small Ring Compounds

process, temp, activation energy (kJ)	$\Delta H$ (ring opening), kJ		consequences
	new bond energies	old bond energies	
cis-trans isomerization of ethylene- $d_2$ , <sup>9</sup> 800 K, 272	266	248	
cis-trans isomerization of 2-butene, <sup>9</sup> 1100 K, 275	275	246	
cis-trans isomerization of 1,2-dideuteriocyclopropane, 700 K, <sup>9</sup> 268	255	238	
dec of cyclopropane to propylene, 700 K, <sup>9</sup> 272			1,2 H migration has activation barrier of 17 kJ as against 34 kJ using old bond energies
trans-cis isomerization of 1,2-dimethyl-1,2-bis(trideuteriomethyl)cyclopropane, 600 K, 228 <sup>50</sup>	232	202	
dec of 1,1,2,2-tetramethylcyclopropane to 2,4-dimethylpentene-2, 1100 K, <sup>1</sup> 260			1,2 H migration has barrier of 28 kJ as against 58 kJ using old bond energies
trans-cis isomerization of 1,2-dimethylcyclobutane, 700 K, <sup>9</sup> 257	263	235	
dec of 1,2-dimethylcyclobutane to propylene, 700 K, <sup>9</sup> 258			barrier of $\beta$ -bond scission is close to zero as against 23 kJ using old bond energies

$\Delta H_f(t\text{-C}_4\text{H}_9\cdot) = 38.3$  kJ/mol on the basis of  $S(t\text{-C}_4\text{H}_9) = 310$  J/K mol. For the zero-barrier case,  $S(t\text{-C}_4\text{H}_9\cdot) = 320$  J/K mol. This leads to 41.5 kJ/mol. There is thus a clear 8 to 10 kJ/mol discrepancy. This is two to three times larger than the estimated experimental uncertainty.

It will be noted that unlike the other systems where there is very little scatter, the high-temperature data for *tert*-butyl radicals are divided into two groups. One set of results involving neopentane decomposition yields bond dissociation energies slightly higher than 406 kJ, while the other set from hexamethylethane decomposition gives bond dissociation energies in the 401 kJ range. It is indicative of the possibility that there are uncertainties that we have not accounted for. For example, the thermodynamic properties of the stable molecules all have some degree of error since they are all based on lower temperature measurements.

### Radical Decomposition Rates

When combined with the activation energies for the addition of methyl or H atoms to the appropriate olefins, activation energies for radical decomposition can be derived. These are summarized in Table III. An examination of the rate expressions reveals some interesting tendencies. The  $A$  factors are all in the "normal" range and thus indicative of a transition state that is similar to that of the radical. In the two cases of C-C bond cleavage the entropies of activation vary by only 2 J/K-mol. In the case of C-H bond cleavage variations are somewhat larger than that due to reaction path degeneracies alone. Methyl substitution at the  $\alpha$  and  $\beta$  positions changes the activation energy by no more than 10 kJ. These general trends are supported by information from other systems. Thus our recent analysis of ethyl radical decomposition<sup>39</sup> yielded the rate expression  $k(\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}) = 10^{13.4} \exp(-19306/T)$  at 600 K. This is close to what could have been expected on the basis of our results for isopropyl and *tert*-butyl radical decomposition. In an earlier study on *sec*-butyl radical decomposition we have found<sup>47</sup> the branching ratio for methyl vs. hydrogen ejection to be 12 to 1 at 1100 K. The ratio derived from Table III is 7 to 1. This can be considered to be good agreement since at elevated temperatures reactions are in the fall-off region and under weak collision conditions (argon) the lower energy decomposition channel will be favored. Information

on the decomposition of *tert*-amyl radicals can be derived from the decomposition of 3,3-dimethylpentane.<sup>1</sup> Using a heat of formation of the ethyl radical of 119 kJ/mol (298 K) we find  $\Delta H_f(\text{tert-amyl}) = 32.6$  kJ/mol at 298 K. Combining this value with the entropy of *tert*-amyl radical as tabulated on Table II and the evaluated rate expression for methyl addition to isobutene<sup>10</sup>  $k(\text{CH}_3 + i\text{-C}_4\text{H}_8 \rightarrow \text{tert-amyl}) = 10^{8.15} \exp(-3474/T)$  L/mol-s, we find for the reverse process  $k(\text{tert-amyl} \rightarrow i\text{-C}_4\text{H}_8 + \text{CH}_3) = 10^{13.03} \exp(-15011/T)/\text{s}$ . This is very close to the values for *n*-propyl and *sec*-butyl radical decomposition. Finally, comparison of the rate constants for isopropyl decomposition with that of the *sec*-butyl radical to 1-butene and an H atom show that the effect of  $\gamma$  substitution is negligible. The general pattern of results thus provides an empirical basis for the prediction of the rate expression for the decomposition of all alkyl radicals.

It is also interesting to note that our heat of formation for *tert*-amyl radical leads to  $D(\text{tert-amyl-H}) = 402.5$  kJ/mol which is very close to the value for *tert*-butyl. Note that in this case ESR studies<sup>48</sup> have demonstrated that the ethyl rotor has a barrier to internal rotation of only 800 J. This would seem to suggest that the methyl rotors will effectively have no barrier to rotation.

- (35) W. Tsang, *Int. J. Chem. Kinet.*, **10**, 1119 (1978).  
 (36) J. M. Tulloch, M. T. Macpherson, C. A. Morgan, and M. J. Pilling, *J. Phys. Chem.*, **86**, 3812 (1982).  
 (37) W. Tsang In "Shock Waves in Chemistry", A. Lifshitz, Ed.; Marcel Dekker, New York, 1981, p 59.  
 (38) K. R. Bull, R. M. Marshall, and J. H. Purnell, *Proc. R. Soc. London, Ser. A* **342**, 259 (1975).  
 (39) W. Tsang and R. F. Hampson, to be published.  
 (40) J. E. Taylor, D. A. Hutchings, and K. J. Frech, *J. Am. Chem. Soc.*, **91**, 2215 (1969).  
 (41) P. D. Pacey, *Can. J. Chem.*, **51**, 2415 (1973).  
 (42) J. A. Walker and W. Tsang, *Int. J. Chem. Kinet.*, **11**, 867 (1979).  
 (43) R. M. Marshall, H. Purnell, and P. D. Storey, *J. Chem. Soc., Faraday Trans. 1*, **71**, 85 (1975).  
 (44) G. Atri, R. R. Baldwin, G. A. Evans, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, **74**, 366 (1978).  
 (45) F. Baronnet, M. Ozierzynski, G. M. Come, R. Martin, and M. Niclaire, *Int. J. Chem. Kinet.*, **3**, 197 (1971).  
 (46) D. Griller and K. Ingold, *Int. J. Chem. Kinet.*, **6**, 453 (1974).  
 (47) W. Tsang, *J. Phys. Chem.*, **76**, 143 (1972).  
 (48) H. Fischer In "Free Radicals", Vol. 2, J. K. Kochi, Ed.; Wiley New York, 1973, p 483.



On this basis, it is difficult to justify a barrier to rotation for the methyl groups in *tert*-butyl.

### Consequences

The higher heats of formation or bond dissociation energies proposed here have important implications with respect to our understanding, at a fundamental level, of hydrocarbon cracking to olefins. With the available data base and thermokinetic considerations we have the basis for the complete quantitative description of the breakdown process in terms of elementary single-step reactions. In a sense this represents the "ultimate" chemical explanation of the phenomena. Indeed, the present results suggests that the data base for such understanding has existed for many years.

With these present results there can no longer be any doubt regarding the virtual absence of a barrier to ring closure for the cyclization of small hydrocarbon diradicals. Summarizing briefly, the enthalpy for ring opening during the decomposition of small ring compounds can be written as<sup>49</sup>

$$\Delta H(\text{ring opening}) = 2\Delta H(\text{alkane} \rightarrow \text{alkyl} + \text{H}) - \Delta H(\text{H}_2 \rightarrow 2\text{H}) + \Delta H(\text{hydrogenation, cyclane})$$

where the alkane is  $\text{HC}_n\text{H}_{2n}\text{H}$  and the cyclane is  $\text{C}_n\text{H}_{2n}$ . Data for a number of representative compounds can be found in Table V. Also included are results on the *cis*-*trans* isomerization of olefins. Following Bergman,<sup>49</sup> we are treating these substances as a two-membered ring. There is very satisfactory agreement between the activation energy for ring opening and calculated results. Barriers to ring closing are reduced drastically. This is in striking contrast to the situation when the older bond energies are used. Bergman<sup>49</sup> and Berson<sup>50</sup> have discussed in detail the unreasonableness of the assumption of the barrier. A necessary consequence of the present results is a large reduction in the barrier

(49) R. Bergman In "Free Radicals", Vol. 1, J. K. Kochi, Ed.; Wiley, New York, 1973, p 191.

(50) J. Berson In "Annual Reviews of Physical Chemistry", Annual Reviews, Inc. Palo Alto, CA, 1977, p 111.

to 1-2 hydrogen migration for the trimethylene radical during decomposition. The rates are thus much faster. Since these are fundamentally disproportionation reactions, this is to be expected. In the case of the tetramethylene diradical, the rate of  $\beta$ -bond scission is also increased since there is now no barrier to decomposition. This is in line with the tendency of the product olefins to retain some degree of the original conformation. With the older bond energies it is necessary to postulate a high barrier to internal rotation in order to rationalize the results. This is contrary to the expectation of minimal barriers to rotation of such systems.

### Conclusions

The generally conviction that measurements of the rate constants for alkyl radical decomposition suffer from gross errors is not correct. The misconception arises from an underestimation of the appropriate bond dissociation energies or heats of formation of the radicals in question. The higher values proposed here are supported by all available rate data from hydrocarbon decomposition and radical buffer studies. Results from iodination studies used as the basis for recently recommended values for radical heats of formation<sup>8</sup> lead to the implication that a great portion of the existing kinetic data on hydrocarbon systems which can be brought to bear on this question is in gross (orders of magnitude) error. This is difficult to believe inasmuch as results (from completely different experiments) are replicable. We have not been able to identify the source of error in the iodination experiments. Particularly disturbing is that the discrepancies are all in one direction. Nevertheless, our results suggest that one should be very cautious in the use of bond dissociation energies from iodination studies for quantitative purposes. Certainly, the present results would justify placing a 15 kJ uncertainty limit on many such values.

**Acknowledgment.** This work was supported by the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Science under Interagency Agreement DE-A-101-76PR06010. I am grateful to D. M. Golden, D. F. McMillen, S. Lias, and S. E. Stein for careful reading of the manuscript and many useful comments.

## Chirality of the Electron Density Distribution in Methyl Groups with Local $C_3$ Symmetry

Alberto Gutiérrez, James E. Jackson, and Kurt Mislow\*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. Received October 9, 1984

**Abstract:** The chirotopicity of methyl groups with local  $C_3$  symmetry cannot be expressed in the static point-nuclear distribution. We now report *ab initio* (6-31G) calculations for twisted ethane ( $D_3$ ) and 1,1,1-trifluoroethane ( $C_3$ ) that reveal a chiral distortion of the electron distribution throughout the  $\text{CH}_3$  group. The effect is small but may be implicated in chirality phenomena and chiral discriminations.

Molecular models may be cut into chiral or achiral segments whose symmetries are subgroups of the molecular point group.<sup>1,2</sup> In the general model of the molecule, the local chirality (chirotopicity) of such a segment is observable in the nuclear and electron distribution functions.<sup>2</sup> Where the nuclei form a chiral array, the electron distribution is expected to follow suit. However, under

the assumption of the point-nuclear model, there are cases in which the  $\delta$  distribution of nuclear positions does not allow a distinction between chirotopic and achirotopic subarrays.<sup>3</sup> In such cases the distinction can come from a consideration of the electron distribution. In this paper we show the manifestation of such an effect

(1) Anet, F. A. L.; Miura, S. S.; Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* 1983, 105, 1419. This segmentation is an abstract and purely geometric operation and not a chemical fragmentation.

(2) Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* 1984, 106, 3319.

(3) Let  $m$  be the *minimum* number of points that are required to define a chiral array of points in  $E^3$  ( $m \geq 4$ ). Then  $m$  is equal to the order of the symmetry group for arrays with  $D_n$ ,  $T$ ,  $O$ , or  $I$  symmetry and equal to twice the order of the group for  $C_n$  ( $n > 1$ ) symmetry ( $m = 4$  for  $C_1$ ). For example,  $m = 12$  for  $C_6$ ,  $D_6$ , or  $T$  symmetry.