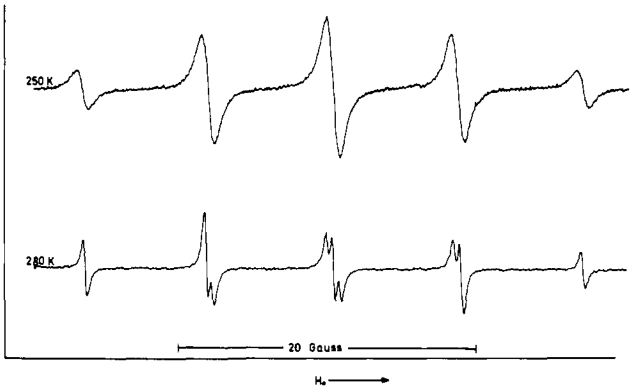

Figure 2. EPR spectra of the $\cdot N(SO_2F)_2$ free radical formed on decomposition of $Xe[N(SO_2F)_2]_2$ in $CFCl_3$.

Bridging Xe–F–Xe stretches are typically quite weak in the Raman effect and occur below 500 cm^{-1}.[38]

EPR of the $\cdot N(SO_2F)_2$ Radical. The thermal decomposition of nearly all xenon(II) compounds of the type FXeA and XeA_2 gives rise to products which are best rationalized on the basis of the formation of the intermediate free radicals A·. These radicals then dimerize or undergo further reactions depending on the nature of A and the conditions. In the decomposition of $FXeN(SO_2F)_2$ and $Xe[N(SO_2F)_2]_2$, $[N(SO_2F)_2]_2$ is formed in high yield. It is reasonable to suppose that this product arises via dimerization of $\cdot N(SO_2F)_2$. To gain support for this supposition, it was planned to photolyze a solution of $Xe[N(SO_2F)_2]_2$ at lower temperature. This turned out to be unnecesary, since surprisingly high concentrations of a radical species were observed in a solution of $Xe[N(SO_2F)_2]_2$ in $CFCl_3$ near 0 °C without photolysis. The EPR spectrum of the radical species is shown in Figure 2 at 250 and 280 K. The spectra are clearly explicable in terms of the $N(SO_2F)_2$ radical.

The five-line spectrum at 250 K with $a_{iso} = 8.3$ G and $g = 2.0063$ has peak heights of 1:3:4:3:1. This intensity ratio is expected for a species in which one unpaired electron interacts with one nucleus of spin $I = 1$ and two nuclei of spin $I = {}^1/_2$ and identical coupling constants for all nuclei. At higher temperatures, these lines show additional splitting. At 280 K, the nine-line spectrum can be exactly simulated by assuming that the unpaired electron interacts with one nitrogen and two equivalent fluorine nuclei. The isotropic hyperfine coupling constants are $A_N = 8.4$ and $A_F = 8.0$ G. Both the nitrogen and fluorine splittings are very small compared to related radicals such as NF_2,[40] $N(SO_3)_2$,[2-41] and $ON(SO_3)_2$.[2-42] This suggests that the unpaired electron is strongly delocalized and that the radical is probably planar.[43]

The properties of the $\cdot N(SO_2F)_2$ radical are probably related to the thermal stability of $FXeN(SO_2F)_2$ and $Xe[N(SO_2F)_2]_2$. The latter has much lower stability, and this is similar to the behavior of $FXeOSO_2F$ and $Xe(OSO_2F)_2$.[26] However, the thermal stabilities of $Xe(OSeF_5)_2$ and $Xe(OTeF_5)_2$ are both quite high. The $\cdot N(SO_2F)_2$ and $FSO_3\cdot$[44] free radicals are rather stable and easily observed at higher temperatures, whereas $\cdot OSeF_5$ and $\cdot OTeF_5$ have very short lifetimes in solution above −150 °C.[45] It can be argued that in $\cdot OTeF_5$ and $\cdot OSeF_5$, the unpaired electron is more localized on oxygen, favoring dimerization. On the other hand, $\cdot N(SO_2F)_2$ and $FSO_3\cdot$ appear to have the unpaired electron more delocalized. These differences can then have a marked effect on the activation energy for decomposition. The more ionic nature of $FXeN(SO_2F)_2$ and $FXeOSO_2F$ clearly raises the barrier to decomposition.

Conclusion

The ability of xenon to bond to a nitrogen atom of an electronegative ligand has been established in the compounds $FXeN(SO_2F)_2$, $Xe[N(SO_2F)_2]_2$, and $[(FSO_2)_2NXe]_2F^+AsF_6^-$. It was hoped that the discovery of $FXeN(SO_2F)_2$ in 1974 would lead to new advances in the chemistry of xenon with additional examples of new xenon–element bonds and a variety of xenon–nitrogen compounds. These hopes have not yet been realized to any great extent. It is obvious that the number of ligands possessing the necessary but still ill-defined properties needed to stabilize a xenon–element bond is very small. We hope to report on additional new examples of xenon–element bonds in the future and perhaps an example of a xenon–nitrogen multiple bond.

Acknowledgment. The support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation is gratefully acknowledged. The Alexander von Humboldt Stifting and the Alfred P. Sloan Foundation are also acknowledged for research fellowships to D.D.D.

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Rate Constants and Arrhenius Parameters for the Reactions of Primary, Secondary, and Tertiary Alkyl Radicals with Tri-*n*-butyltin Hydride[1]

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Abstract: Rate constants for the title reactions have been measured over a range of temperatures by using laser flash photolytic techniques. At 300 K the rate constants are $10._8$, 2.0_1, 2.3_4, 1.3_5, 2.4_7, and $1.8_4 \times 10^6$ M^{-1} s^{-1} for methyl, ethyl, *n*-butyl, isopropyl, cyclohexyl, and *tert*-butyl, respectively. The Arrhenius preexponential factors range from $10^{9.39}$ M^{-1} s^{-1} for methyl to $10^{8.43}$ M^{-1} s^{-1} for *tert*-butyl and activation energies from 3.97 kcal/mol for cyclohexyl to 2.95 kcal/mol for *tert*-butyl. The rate constant (k_{10}) for the 1,5-cyclization of 5-hexenyl radical to cyclopentylmethyl radical can be represented by $\log k_{10}/s^{-1} = (10.37 \pm 0.32) - (6.85 \pm 0.42)/\theta$, where $\theta = 2.3RT$ kcal/mol.

The reactions of carbon-centered radicals with triorganotin hydrides are of considerable importance in organic chemistry. Probably the best known and most useful reaction is the reduction of alkyl halides, RX, to the hydrocarbon, RH, with tri-*n*-butyltin

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hydride. This reaction involves a two-step free radical chain process.[3]

$$\mathrm{R\cdot} + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k_1} \mathrm{RH} + n\text{-}\mathrm{Bu_3Sn\cdot} \quad (1)$$

$$n\text{-}\mathrm{Bu_3Sn\cdot} + \mathrm{RX} \rightarrow n\text{-}\mathrm{Bu_3SnX} + \mathrm{R\cdot} \quad (2)$$

In 1968[4] rate constants for reaction 1, k_1 were determined at room temperature (ca. 298 K) by the classical rotating sector technique for R = methyl, *n*-hexyl, cyclohexyl, and *tert*-butyl (k_1 = 5.8, 1.0, 1.2, and 0.74 × 10^6 M^{-1} s^{-1}, respectively). The only direct confirmation that these values were of the correct order of magnitude was provided in 1980[5] when it was shown that the tertiary alkyl center in the type II biradical derived from γ-methylvalerophenone reacted with *n*-Bu_3SnH with a rate constant of 1.1 × 10^6 M^{-1} s^{-1} at ca. 295 K. Nevertheless, the 1968 rate constants have been widely used in competitive studies in order to obtain the rate constants for other processes, particularly rate constants for the unimolecular rearrangements (e.g., ring openings and closings) of carbon-centered radicals.[6] Since many of these competitive experiments have been carried out at temperatures far from ambient, there has been for some time an urgent need to obtain the Arrhenius parameters for reaction 1 and, incidentally, to check the validity of the original rate constants.

The current availability of pulsed time resolved techniques, and the recent characterization of the tri-*n*-butylstannyl radical using transient absorption spectroscopy,[7] should make it possible to obtain k_1 values by laser flash photolysis *provided* a suitable photochemical reaction for generating alkyl radicals can be found. Such a source of alkyl radicals must (i) only require excitation at a sufficiently long wavelength that the *n*-Bu_3SnH is transparent, (ii) produce radicals in a fast process ($\tau < 20$ ns), (iii) not involve precursors which are reactive toward alkyl or stannyl radicals, and (iv) occur with a high quantum yield (preferable >0.2). Few "conventional" sources of alkyl radicals fulfill these conditions, and finding a suitable system, adaptable to a variety of alkyl radicals, proved surprisingly difficult. The eventual solution[8] was to react *tert*-butoxyl radicals with trialkylphosphines or arsines—reactions which have received considerable attention, particularly by ESR spectroscopists, in recent years.[9]

Results

Generation of R·. All the results reported herein have been obtained by laser flash photolytic techniques employing the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser for excitation. All experiments were carried out under oxygen-free conditions.

The reactions used as the alkyl radical sources involve an S_H2 process[10]

$$\mathrm{(CH_3)_3COOC(CH_3)_3} \xrightarrow{h\nu} \mathrm{2(CH_3)_3CO\cdot} \quad (3)$$

$$\mathrm{(CH_3)_3CO\cdot} + \mathrm{R_3M} \rightarrow \mathrm{R_3\dot{M}OC(CH_3)_3} \quad (4)$$

$$\mathrm{R_3\dot{M}OC(CH_3)_3} \rightarrow \mathrm{R\cdot} + \mathrm{R_2MOC(CH_3)_3} \quad (5)$$

$$\mathrm{M = P,\ As}$$

at the metalloid center of a trialkylphosphine or arsine. For this system to be useful, reactions 4 and 5 must be extremely rapid so that alkyl radical generation is at least 10 times faster than their decay by reaction 1.[11] Reaction 4 is known to be fast for a variety of trivalent phosphorus compounds,[12,13] and we have now extended this earlier work to include some of the substrates used in the present study. Values of k_4 were obtained at room temperature by using diphenylmethanol as a probe—a technique which has been described in detail in earlier publications.[12-14] The results are summarized in Table I, which also includes some related rate constants from the literature.

Table I. Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Some Trivalent Phosphorus Compounds at Room Temperature[a]

substrate	k_4, M^{-1} s^{-1}	ref
Et_3P[b]	1.2 × 10^9	12
n-Bu_3P[c]	6.5 × 10^8	this work
t-Bu_3P[c]	5.2 × 10^8	this work
$(C_6H_5CH_2)_3P$[c]	5.8 × 10^8	this work
$(C_6H_5)_3P$[d]	1.9 × 10^9	12
$C_6H_5P(OEt)_2$[d]	1.4 × 10^9	13
$(EtO)_3P$[b]	8.1 × 10^8	12
$(EtO)_3P$[d]	1.7 × 10^9	13

[a] By laser flash photolysis unless otherwise noted. [b] By an EPR spectroscopic competitive procedure. [c] Using diphenylmethanol as the probe. [d] By monitoring the growth of the phosphoranyl radical.

Since the reaction mixture will contain both the R_3M alkyl radical source and *n*-BuSnH and since both are very reactive toward *tert*-butoxyls, it is important to work under conditions where the majority of the *tert*-butoxyls are trapped by R_3M, i.e., by reaction 4 rather than reaction 6. The rate constant for

$$\mathrm{(CH_3)_3CO\cdot} + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k_6} \mathrm{(CH_3)_3COH} + n\text{-}\mathrm{Bu_3Sn\cdot} \quad (6)$$

reaction 6 is 2 × 10^8 M^{-1} s^{-1} at 295 K,[7] and k_4 is ca. 10^9 M^{-1} s^{-1} (see Table I). If two-thirds or more of the *tert*-butoxyls are to be trapped by the R_3M, then the $[R_3M]/[n\text{-}Bu_3SnH]$ ratio must be ≥0.4.

Reaction 5 is also required to occur in the nanosecond time scale. A recent kinetic study[13] of the α scission of *n*-$Bu_3\dot{P}OC(CH_3)_3$ (see eq 7) yielded the Arrhenius parameters, log A_7/s^{-1}

$$n\text{-}\mathrm{Bu_3\dot{P}OC(CH_3)_3} \rightarrow n\text{-}\mathrm{Bu_2POC(CH_3)_3} + n\text{-}\mathrm{Bu\cdot} \quad (7)$$

= 12.7 and E_7 = 5.74 kcal/mol, from which k_7 (=k_5) can be calculated to be 2.9 × 10^8 s^{-1} at 300 K. The α scission of other $R_3\dot{P}OC(CH_3)_3$ radicals should be equally facile for R = *n*-alkyl[15] and should be much faster for R = benzyl, *sec*-alkyl, or *tert*-alkyl. However, the $(CH_3)_3\dot{P}OC(CH_3)_3$ radical must be much more resistant to α scission since it can be detected by EPR spectroscopy up to at least 253 K.[15,16] For this radical k_5 has been measured and found to have a value of 32.3 s^{-1} at 173 K in cyclopropane.[16,18] Assuming that log A_5/s^{-1} is 12.7 for this reaction[19] yields E_5 = 8.85 kcal/mol and k_5 = 1.8 × 10^6 s^{-1} at 300 K, which means that

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(1) Issued as N.R.C.C. No. 19776.

(2) N.R.C.C. Research Associate 1979–1981.

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(11) While this is not an absolute requirement, systems which do not meet this criterion are poor candidates for kinetic studies.

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(15) For example, for R = ethyl the value of k_5 has been estimated[16] to be ca. 10^3 s^{-1} at 128 K from the fact that $Et_3\dot{P}OC(CH_3)_3$ is just detectable at this temperature.[17] At 128 K, k_7 (R = *n*-Bu) is calculated to be 8 × 10^2 s^{-1} from the Arrhenius parameters given in the text.

(16) Cooper, J. W.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1976**, 808–813.

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(18) The rate constant is smaller in toluene, probably because of cage return.[16] If the methyl radicals formed in this α scission react with the phosphoranyl, then the true value of k_5 will be only 16.15 s^{-1}.

(19) The measured value was 8.2 but it was pointed out that this was unreliable.[16]

Table II. Kinetic Parameters for the Reactions of Some Alkyl Radicals (Generated from R_3M) with *n*-Bu_3SnH in Isooctane–Di-*tert*-butyl Peroxide

radical (M)	temp range, K	log $A/M^{-1}\ s^{-1}$ [a]	E,[a] kcal/mol	$10^{-6}k_1$, $M^{-1}\ s^{-1}$ at 300 K	k_1^H/k_1^D at 300 K
methyl (As)	231–317	9.39 ± 0.28	3.23 ± 0.34	$10._6$	2.3
ethyl (As)	248–346	9.14 ± 0.42	3.80 ± 0.57	2.3_0	1.9
n-butyl (P)	245–355	9.06 ± 0.31[b]	3.65 ± 0.41[b]	2.4_7	2.3
isopropyl (P)	251–358	8.71 ± 0.37	3.47 ± 0.49	1.5_0	
cyclohexyl (P)	300–355[c]	9.24 ± 0.78	3.97 ± 1.15	2.1_9	
tert-butyl (P)	263–351	8.43 ± 0.14	2.95 ± 0.19	1.8_7	

[a] Error limits represent 95% confidence. [b] For the reaction with *n*-Bu_3SnD the relation $\log k_1^D/M^{-1}\ s^{-1} = (8.63 \pm 1.06) - (3.48 \pm 1.43)/\theta$ was obtained which gives $k_1^D = 1.2_0 \times 10^6\ M^{-1}\ s^{-1}$ at 300 K. [c] Small temperature range dictated by solubility.

the α scission of $(CH_3)_3\dot{P}OC(CH_3)_3$ is too slow a source of methyl radicals to be useful in our experiments. Fortunately, $(CH_3)_3\dot{A}sOC(CH_3)_3$ does not suffer from this difficulty, the radical undergoing α scission so rapidly that it cannot be detected by EPR spectroscopy even at low temperatures.[20] In addition, we have found that trialkylarsines are more reactive toward *tert*-butoxyls than are the analogous phosphines;[21] e.g., for Et_3As, $k_4 = 2.5 \times 10^9\ M^{-1}\ s^{-1}$ at 298 K. Exploratory work with triethylarsine revealed no unexpected problems, and so trimethylarsine was used as our source of methyl radicals. It proved to be completely satisfactory. It should be added that the β scission reaction (which would yield $R_3M{=}O + (CH_3)_3C\cdot$) is not expected to compete with the α scission for any of the phosphines or arsines studied in this work.[9]

Finally, in order to work under conditions where our instrument has optimum response, we require that $k_1[n\text{-}Bu_3SnH] \geq 2 \times 10^5\ s^{-1}$ and we must employ di-*tert*-butyl peroxide concentrations of at least 1 M since this compound is a poor chromophore at the excitation wavelength ($\epsilon_{337} = 0.30\ M^{-1}\ cm^{-1}$). Somewhat to our own surprise, all the conditions required to study reaction 1 could be met for all the alkyl radicals we investigated except benzyl (vide infra) although the concentrations of all the substrates used had, in general to be quite high. Since all of the alkyl radical–tin hydride reactions proceed at rates which are substantially slower than diffusion control and since all the components in our reaction mixture are nonpolar and hydrocarbon-like, we believe that the rate constants measured in this work can be utilized in virtually any solvent in which *n*-Bu_3SnH has been, or is likely to be, employed in competitive kinetic studies.

Measurements of k_1. These measurements were carried out by monitoring the transient absorptions produced when samples containing $(CH_3)_3COOC(CH_3)_3$ (~500 μL), R_3M (~500 μL), and *n*-Bu_3SnH in isooctane (500-μL total, with the *n*-Bu_3SnH equal to 100, 200, 300, 400, and 500 μL) were excited by the laser pulse. This pulse is absorbed by the peroxide which undergoes a fast and efficient decomposition[14] (reaction 3). The sequence of reactions 3, 4, and 5 produces the alkyl radicals which then undergo reaction 1 to yield the detectable species *n*-$Bu_3Sn\cdot$. The buildup of the signal due to the *n*-$Bu_3Sn\cdot$ follows pseudo-first-order kinetics (see insert in Figure 1), and an experimental rate constant, k_{exptl}, can be derived according to eq 8, where A_∞ and A_t are the

$$\ln\,(A_\infty/(A_\infty - A_t)) = k_{\text{exptl}}t \tag{8}$$

optical densities in the plateau region and at time t, respectively (see Figure 1). The value of k_{exptl} is a composite of all pseudo-first-order processes in which the alkyl radicals participate, i.e.,

$$k_{\text{exptl}} = \tau_R^{-1} + k_1[n\text{-}Bu_3SnH] \tag{9}$$

where τ_R is the lifetime of the alkyl radical in the solvent mixture without *n*-Bu_3SnH and excludes second-order processes. These need to be prevented by working at appropriately low doses. The technique used to determine a suitable range of doses has been described elsewhere.[14] The values of k_1 are then derived from a plot of k_{exptl} vs. [*n*-Bu_3SnH]. A representative example is shown in Figure 1.

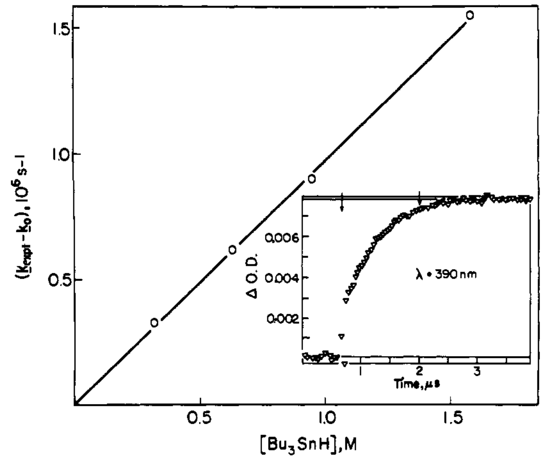

Figure 1. Plot of the experimental rate constant k_{exptl} (corrected for $k_0 \equiv \tau_R^{-1}$) for the reaction of *tert*-butyl (from $(t\text{-}Bu)_3P$) and *n*-Bu_3SnH at 263 K. Insert: Representative trace monitored at 390 nm for [*n*-Bu_3SnH] = 1.58 M. (Note the initial jump due to the occurrence of reaction 6. The section between the arrows corresponds to the points used for kinetic calculations).

The insert in Figure 1 shows a small jump immediately after excitation. A spectroscopic examination at this time showed the *n*-$Bu_3Sn\cdot$ spectrum which, except for its intensity, was identical with that recorded in the plateau region. We attribute this small jump to the occurrence of reaction 6 which does not affect the kinetic analysis since it merely produces a vertical offset of the signal. The jump was most pronounced at high *n*-Bu_3SnH concentrations, as would be expected.

Measurements of k_1 were made for each of six alkyl radicals at five to nine different temperatures over as wide a temperature range as possible. These results are summarized in Table II. The full kinetic data are available as supplementary material. A few measurements were also made of the rate constant for deuterium abstraction from *n*-Bu_3SnD (see footnote *b*, Table II).

Our attempts to measure k_1 for benzyl radicals were completely unsuccessful. This was not because the *tert*-butoxyl–tribenzylphosphine reaction was unduly slow (see Table I), nor was it due to this reaction taking an unexpected course or to α scission being unexpectedly slow because, on monitoring for benzyl radicals in this system at 317 nm,[22] their efficient production was confirmed. We therefore conclude that the benzyl radical–*n*-Bu_3SnH reaction is relatively slow and that at room temperature k_1 must be $\leq 3 \times 10^5\ M^{-1}\ s^{-1}$.

Discussion

The k_1 values obtained in the present work for R = methyl, *n*-alkyl, cyclohexyl, and *tert*-butyl at ambient temperatures are, on average, twice as large as the values originally obtained[4] (cf. Introduction and Table II). This degree of agreement is extremely gratifying in view of the well-known difficulties associated with the rotating sector method. Moreover, conclusions reached by

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(21) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C., unpublished results.

(22) At which wavelength they can be readily detected ($\epsilon \approx 10\,000\ M^{-1}\ cm^{-1}$, see: Habersbergerová, A.; Janovský, I.; Teplý, J. *Radiat. Res. Rev.* **1968**, *1*, 109–181.

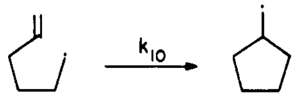
using *n*-Bu_3SnH as a hydrogen donor in competitive studies of alkyl radical rearrangements[6] at ambient temperatures are largely reaffirmed.

The most intriguing result (and one which confirms the earlier data)[4,5] is that the rate constants for the reactions of primary, secondary, and tertiary alkyl radicals with *n*-Bu_3SnH are essentially equal at room temperature. This is a convenient property which makes reaction 1 even more useful as a standard for determining the values of the rate constants for other alkyl radical reactions since, within reasonable limits, k_1 will not depend on the detailed structure of the alkyl radical. Only methyl (and presumably other reactive alkyls such as cyclopropyl) and benzyl (and presumably other resonance-stabilized alkyls such as allyl) have k_1 values at room temperature that differ significantly from $2 \times 10^6\ M^{-1}\ s^{-1}$.

The Arrhenius preexponential factors all lie in the expected range and show (with the possible exception of cyclohexyl) the anticipated decrease with increasing steric hindrance of the attacking alkyl radical. The activation energies for the isopropyl and *tert*-butyl radical reactions seem to be anomalously low, which one is tempted to attribute to "polar factors".

The deuterium kinetic isotope effects found in this work lie between those we reported earlier (viz.,[4] 2.7 and 2.8 for cyclohexyl and *tert*-butyl, respectively) and those reported by Kozuka and Lewis[23] (e.g., 1.6 ± 0.1 for cyclohexyl at 298 K). They are, however, in good agreement with the deuterium isotope effects which can be calculated from Kozuka and Lewis' measured tritium isotope effects (e.g., 2.25 for *n*-hexyl at 295 K).

Finally, we note that quite a large amount of kinetic data in the literature requires minor (or occasionally major) revision as a result of the present work. For brevity, we will confine ourselves to the 5-hexenyl radical cyclization which has become by far the most widely used primary alkyl radical clock reaction.[6,24]



(10)

The Arrhenius parameters for this reaction have twice been determined in this laboratory by kinetic EPR spectroscopy: viz.,[25,26] $\log A_{10}/s^{-1} = 10.7 \pm 1.0$[25] and 9.5 ± 1.0;[26] $E_{10} = 7.8 \pm 1.0$[25] and 6.1 ± 1.0 kcal/mol.[26] These data have then been used to calculate the Arrhenius parameters for reaction 1 from the yields of 1-hexene and methylcyclopentane produced when this 1,5 cyclization competes with the hydrogen abstraction from *n*-Bu_3SnH (and these data have then, in turn, been used to calculate rate constants for other alkyl radical rearrangements). The 5-hexenyl radical/*n*-Bu_3SnH reaction has been examined on several occasions.[27-31] The most reliable data[31] indicate that $\log (A_{10}/A_1) = 1.30 \pm 0.08$ and $E_{10} - E_1 = 3.16 \pm 0.10$ kcal/mol. The best Arrhenius equation to use for the reaction of a primary alkyl radical with *n*-BuSnH would seem to be that which can be obtained by combining the data for the ethyl radical/*n*-Bu_3SnH reaction with that for the *n*-butyl/*n*-Bu_3SnH reaction, viz.

$$\log k_1/M^{-1}\ s^{-1}\ (\text{primary alkyl}) = (9.07 \pm 0.24) - (3.69 \pm 0.32)/\theta \quad (11)$$

where $\theta = 2.3\ RT$ kcal/mol. Combining eq 11 with the $\log (A_{10}/A_1)$ and $E_{10} - E_1$ values given above yields the Arrhenius equation for the 5-hexenyl cyclization

$$\log k_{10}/s^{-1} = (10.42 \pm 0.32) - (6.85 \pm 0.42)/\theta \quad (12)$$

where the errors represent 95% confidence limits. We believe this Arrhenius equation is highly reliable (compared with earlier EPR derived equations) and recommend that it be used henceforth in all quantitative studies involving the 5-hexenyl radical.

Experimental Section

Materials. All compounds used in this work were obtained commercially. With only a few exceptions, they were carefully purified, generally by high vacuum distillation, and stored under N_2 before use.

Techique. Our instrument makes use of the pulses from a Molectron UV-24 nitrogen laser for excitation. The system has a variable-temperature insert and controller similar to those used in EPR spectroscopy. The instrument has been fully interfaced with a PDP 11/03L computer which controls the experiment, gathers the data, and provides suitable storage and processing devices. Further details have been given elsewhere.[32]

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Supplementary Material Available: Seven tables (Table III–IX) giving detailed kinetic data (18 pages). Ordering information is given on any current masthead page.

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