

tionless decay is probably governed largely by the radiationless decay modes available to the substrate triplet.⁴²

As will be reported in detail elsewhere, there is a correlation between the calculated C-T-state energy and whether a two- or three-component exciplex is formed. The relatively shorter lived two-component exciplex is generally the only species detected when the calculated C-T state lies energetically close to or lower than the substrate triplet; in other cases, the three-component SQ₂ exciplex is formed. A reasonable explanation for this behavior is that a complex having stronger C-T contributions (the 1:1 exciplex) should have additional radiationless decay paths, while the complexes in which these contributions are less important (the 1:2 exciplexes) should have radiationless decay paths (and hence rates) similar to those of the substrate excited state.

(42) In addition to pathways available in the substrate, entirely new pathways which are inherent only to the exciplex may come into play. For example, if the quencher has heavy atom substituents, then catalysis of intersystem crossing could accompany or compete with the effects mentioned above.⁴³⁻⁴⁵

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The interactions between excited substrate and quenchers in nonpolar media where limited donor-acceptor interaction occurs, as exemplified by the present results, should probably be a fairly general phenomenon, especially for relatively long-lived triplet states. Interesting examples which may be related to the present phenomenon include the gas-phase excited-state quenching reported by Thayer and Yardley⁴⁶ where quenching rate correlations with electron affinity are observed, yet the quenching process almost surely does not involve electron transfer and the solution complexes between dipolar excited states and small polar molecules reported by Chandross.⁴⁷ It is easy to conceive of a continuum extending from specifically detectable quenching to subtle effects of the solvent on excited-state lifetimes.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XVI. Cyclization of the 5-Hexenyl Radical¹

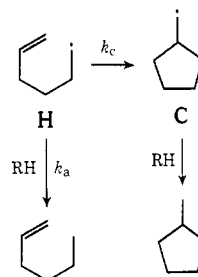
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Abstract: The rate constant, k_c , for cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical has been measured from -45 to -85° by an epr spectroscopic technique. It can be represented by $\log(k_c/\text{sec}^{-1}) = (10.7 \pm 1.0) - (7.8 \pm 1.0)/\theta$, where $\theta = 2.3RT$ kcal/mol. Extrapolation of this equation yields $k_c = 1 \times 10^5 \text{ sec}^{-1}$ at 25° , in excellent agreement with an earlier estimate.

Many investigators have shown that 5-hexenyl radicals, H, cyclize *irreversibly* to yield cyclopentylmethyl radicals, C.⁴⁻⁷ The 5-hexenyl radical has become of prime importance in studies of the kinetic properties of non-resonance-stabilized, unhindered, primary alkyl radicals. It has proven particularly useful in atom transfer studies.^{4-6,8-10} For example, in the

presence of a suitable donor, RH, both 1-hexene and methylcyclopentane may be produced. The relative



concentrations of these two hydrocarbons depend only on the concentration of RH and the rate constant ratio, k_a/k_c . Provided k_c is known, a product analysis will yield k_a for 5-hexenyl and, logically, for any other simple primary alkyl radical.

The only usable value for k_c is an estimate from these laboratories⁹ of 10^5 sec^{-1} at $25-40^\circ$. This value was

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(5) J. W. Wilt in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, p 333.

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(7) Some cyclohexyl radicals are also formed at elevated temperatures.^{4,5}

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based on kinetic data⁹ for the reaction of *n*-hexyl bromide with tri-*n*-butyltin hydride at 25° and product data^{8,10} for the reaction of 5-hexenyl bromide with the same tin hydride at 40°. Our value of k_c has received some support from an estimated upper limit of $7 \times 10^5 \text{ sec}^{-1}$ at 25° based on the products of the reaction of 5-hexenyl fluoride with sodium naphthalene.¹¹ In deriving this limiting value, it was necessary¹¹ to assume that the radical was reduced by the sodium naphthalene in a diffusion-controlled reaction.

In this paper we report values of k_c measured by an epr spectroscopic technique over a temperature range from -45 to -85°. Extrapolation to 25° yields a k_c value in agreement with our previous estimate. Application of the 5-hexenyl cyclization to kinetic studies therefore need no longer be restricted to room temperature.

Experimental Section

Materials. Isopentane, di-*tert*-butyl peroxide, trimethylsilane, and hexamethylditin were commercially available materials that were purified by normal procedures before use. 5-Hexenyl bromide (Aldrich) contained ca. 4% *n*-hexyl bromide which could not be removed, even by preparative vpc. For this reason, the measured concentrations of 5-hexenyl were corrected by subtracting 4% of the total alkyl radical concentration, *i.e.*, $[H]_{\text{cor}} = [H] - 0.04 \cdot ([H] + [C])$. All preparations were carried out under argon.

Tris(5-hexenyl)borane was prepared by the procedure of Lyle, *et al.*¹² This material polymerized slowly on standing at room temperature. Even when freshly prepared, the nmr spectrum showed a notable deficiency of vinylic protons (4.8–6.3 ppm downfield from TMS) relative to paraffinic protons (0.6–2.4 ppm), *e.g.*, $[\text{CH}_2=\text{CH-}]/[\text{CH}_2] = 1.7/8$ instead of the required 3/8.

Tris(5-hexenyl)phosphine. 5-Hexenyl bromide (80 g) in 200 ml of dry ether was slowly added to 12.4 g of magnesium in 100 ml of dry ether at room temperature. The Grignard reaction proceeded smoothly. The solution was then cooled in an ice bath, while 16 g of freshly distilled PCl_3 was added slowly. The reaction mixture was treated with saturated aqueous NH_4Cl and the phosphine extracted with ether. It was purified by distillation in a molecular still. The ratio $[\text{CH}_2=\text{CH-}]/[\text{CH}_2]$ was found to be 2.3/8 by nmr. *Anal.* Calcd for $\text{C}_{15}\text{H}_{33}\text{P}$: C, 77.08; H, 11.88. Found: C, 76.87; H, 11.88.

Cyclopentylmethyl bromide was prepared from the alcohol by the procedure of Jenkins and Kochi.¹³

Tris(cyclopentylmethyl)borane was prepared by the reaction of cyclopentylmethylmagnesium bromide with BF_3 in ether at ice temperatures. The reaction mixture was treated with dilute HCl, the supernatant ethereal solution dried, and the ether removed under vacuum. The borane was not purified further. Nmr: three multiplets centered at 1.0, 1.3, and 1.6 ppm downfield from TMS. The product oxidized too readily to allow a reliable analysis for C and H to be made. However, the product must be reasonably pure as photolysis with di-*tert*-butyl peroxide gave only cyclopentylmethyl radicals.

Procedure. Samples were photolyzed in the cavity of a Varian E-4 EPR spectrometer. Radical concentrations were determined by double integration of nonoverlapping lines in the first-derivative epr spectrum, the absolute concentrations being calibrated against DPPH in the usual manner.¹⁴ The kinetic epr technique has been described previously.¹⁴

Results and Discussion

Kochi and coworkers^{15–17} have shown that photolysis

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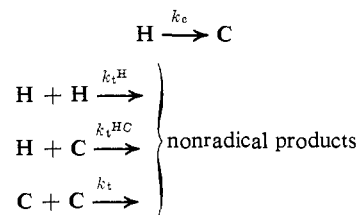
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of solutions of 6-heptenoyl peroxide directly in the cavity of an epr spectrometer yields the 5-hexenyl radical, H, at temperatures of -90° and below. At slightly higher temperatures, both 5-hexenyl and cyclopentylmethyl, C, are observed, while at -35° and above, only the latter is detected. When C was generated independently in separate experiments, it did not give rise to the spectrum of H, confirming that the cyclization reaction is irreversible.

Measurement of the concentrations of H and C formed from some source of H under steady-state conditions can yield the rate constant for cyclization of H, provided the radicals react according to Scheme I.

Scheme I



The usual steady-state treatment^{18–20} yields²¹

$$\frac{1}{[C]} = \frac{2k_t^C[C]}{k_c[H]} + \frac{2k_t^{HC}}{k_c}$$

Since C and H are both primary alkyl radicals, it can be safely assumed^{6,9,22,23} that $k_t^C = k_t^{HC} (= k_t^H)$. Therefore

$$k_c/2k_t^C = ([C]^2/[H]) + [C]$$

and so k_c can be calculated, provided k_t^C is already known or can be independently measured.

Several attempts to generate 5-hexenyl in the epr spectrometer under conditions where this simple kinetic scheme applies were unsuccessful. We did not attempt to use Kochi's method,^{15–17} since acyl peroxides are frequently subject to radical-induced decompositions.²⁴ Instead, we first tried photolyzing solutions of tris(5-hexenyl)borane and di-*tert*-butyl peroxide, a procedure that is usually very satisfactory for alkyl radicals.^{25–27} However, at temperatures above -35°, the relative yield of apparently uncyclized 5-hexenyl was ca. 30% rather than the expected²⁸ 4%. This was undoubtedly

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(21) In this equation $2k_t^C$ appears because two C are destroyed in each C + C reaction; $2k_t^{HC}$ appears, because the cross reaction is, for statistical reasons, twice as likely to occur as either self-reaction.

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due to the loss of 5-hexenyl groups caused by the partial polymerization of the borane during its preparation.

Reaction of 5-hexenyl bromide with trimethylsilyl²⁹ and trimethyltin³⁰ radicals gave good epr spectra of H and C. However, in both of these systems, the concentration of cyclopentylmethyl was proportional to ((light intensity)^{0.6-0.8}), which implies that some C disappear by a kinetically first-order pathway (such as reaction with the silane or hexamethylditin). It is a necessary requirement of the desired kinetic scheme that C disappears only by reaction with a second alkyl radical which, for a photochemical system, means that [C] is proportional to (intensity)^{0.5}.

Photolysis of solutions of di-*tert*-butyl peroxide and tris(5-hexenyl)phosphine in isopentane gave, as expected,^{31,32} strong epr spectra of H and C. The concentration of C was proportional to (intensity)^{0.5} at all temperatures, and the apparent concentration of H reached the expected²⁸ 4% at temperatures above -35°. The only experimental difficulty arose from the rather rapid formation of the long-lived^{32,33} di(5-hexenyl)-di-*tert*-butoxyphosphoranyl, [CH₂=CH(CH₂)₄]₂P[OC(CH₃)₃]₂. However, by allowing the reactants to flow slowly (ca. 0.3 ml/min) through the epr tube,³⁴ the concentration of this phosphoranyl was kept very much lower than the concentrations of H or C. Double integration of appropriate epr spectral lines yielded the concentrations of H (after correction for *n*-hexyl; see Experimental Section) and C listed in Table I. The

Table I. Cyclization of the 5-Hexenyl Radical from Tris(5-hexenyl)phosphine in Isopentane

<i>T</i> , °K	[H] × 10 ⁸ , <i>M</i>	[C] × 10 ⁸ , <i>M</i>	<i>k</i> _c /(2 <i>k</i> _t) ^C × 10 ⁷ , <i>M</i>	(2 <i>k</i> _t) ^C × 10 ⁻⁸ , ^a <i>M</i> ⁻¹ sec ⁻¹	<i>k</i> _c × 10 ⁻² , sec ⁻¹
228	2.5	9.7	4.7	36	17
224	2.7	9.7	4.5	30	13.5
220	3.5	11	4.6	23	11
218	4.0	10	3.5	21	7.4
209	2.7	9.7	4.5	12	5.4
207	4.9	9.4	2.7	10	2.7
199	3.5	7.9	2.6	6.0	1.6
199	4.5	11	3.8	6.0	2.3
195	3.2	8.0	2.8	4.6	1.3
188	8.2	7.0	1.3	2.6	0.34

^a Values obtained by interpolation; see text.

upper temperature limit (-45°) was determined by the *n*-hexyl radicals becoming a significant fraction of the H concentration. The low-temperature limit (-85°) was determined by the excessive broadening of the

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(34) The temperature of the flowing solution was monitored with a thermocouple placed in the epr tube just above the region of photolysis.

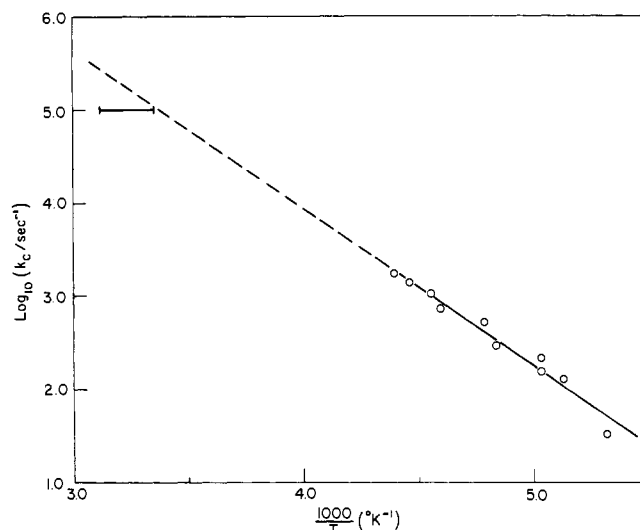


Figure 1. Plot of $\log(k_c/\text{sec}^{-1})$ against $1000/T$ ($^{\circ}\text{K}^{-1}$). The circles represent measurements made in the present work and the bar, the earlier estimate⁹ applicable to temperatures in the range 25-40°.

cyclopentylmethyl epr lines which made measurement of its concentration at even lower temperatures impossible. Values of $k_c/2k_t^C$ calculated from these data are also listed in Table I.

Values of $2k_t^C$ were determined by kinetic epr spectroscopy.^{6,14,20,22} The cyclopentylmethyl radicals were generated by photolysis of isopentane solutions of tris(cyclopentylmethyl)borane and di-*tert*-butyl peroxide having viscosities similar to those of the solutions used in measuring $k_c/2k_t^C$. The experimental values of $2k_t^C$ were: 3×10^{10} at 1°, 1×10^{10} at -26°, 1×10^9 at -54°, and $6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at -83°. These rate constants indicate a substantial activation energy (ca. 5 kcal/mol) for the reaction of two cyclopentylmethyls in this reaction system. Since radical-radical reactions of this type are diffusion-controlled,^{6,22,23} the changes in $2k_t^C$ must be due to changes in the viscosity of the medium.

Combination of the measured values of $k_c/2k_t^C$ with the appropriate interpolated values of $2k_t^C$ yields the rate constants for cyclization of the 5-hexenyl radical listed in Table I and plotted in Figure 1. This rate constant can be represented by

$$\log(k_c/\text{sec}^{-1}) = (10.7 \pm 1.0) - (7.8 \pm 1.0)/\theta$$

where $\theta = 2.3RT$ kcal/mol.³⁵ The preexponential factor is in the range expected for a simple intramolecular cyclization.³⁶ Extrapolation of this equation to room temperature gives a k_c value in excellent agreement with our earlier estimate⁹ (see Figure 1).

The present results should considerably improve the utility of the 5-hexenyl isomerization as a standard for kinetic investigations of primary alkyl radicals.

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