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Hydrogen Abstraction by Biradicals. Reactions with Tri-*n*-butylstannane and Octanethiol

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Abstract: The biradicals generated in the Norrish type II reaction abstract hydrogen atoms from mercaptans and Bu_3SnH with rate constants of 9×10^6 and 1.1×10^6 M^{-1} s^{-1}, respectively (for the biradical from γ-methylvalerophenone). The data from competitive and time-resolved experiments are in excellent agreement. The results suggest that the reactivity of radical sites in biradicals is identical with that of the same sites in monoradicals.

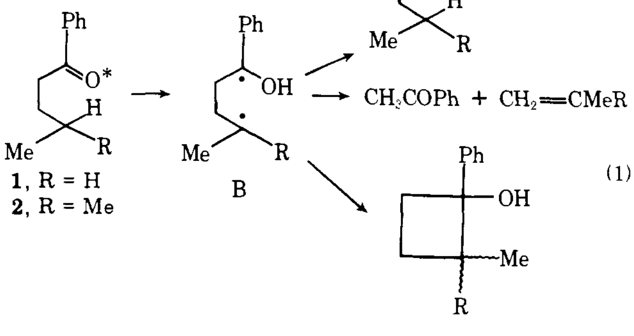
Introduction

Triplet-derived biradicals produced in the Norrish type II reaction have been the subject of several recent studies.[3-10] The first trapping studies were reported in 1972 and involved the abstraction of hydrogen atoms from mercaptans;[3] these studies also led to the first estimate of biradical lifetimes. While mercaptans proved to be excellent biradical scavengers because of their high reactivity toward radical centers and low reactivity toward carbonyl triplets,[11] they also led to considerable uncertainty in the biradical lifetimes because of the unusually large spread in the reported values for the rate constants for the reactions of S–H bonds with carbon-centered radicals.[12] The direct detection of biradicals[7,13] offers now the possibility of a direct, time-resolved measurement of their rates of reaction with mercaptans.

In this paper we report the results of a laser flash photolysis study of the reactions of biradicals generated in the Norrish type II reaction of phenyl alkyl ketones with octanethiol and tri-*n*-butylstannane. We have been able to establish that (a) biradicals react in hydrogen-abstraction reactions with the same rate constants as monoradicals having the same reactive center; (b) the biradical lifetimes obtained from direct or competitive studies are in full agreement if the correct rates of the competitive reactions are known; and (c) we have obtained absolute rate constants for the reactions of secondary and tertiary carbon radical centers with mercaptans.

Results

Our experiments have been carried out using the biradicals generated in the Norrish type II process (reaction 1) of valerophenone (**1**) and γ-methylvalerophenone (**2**).



(1)

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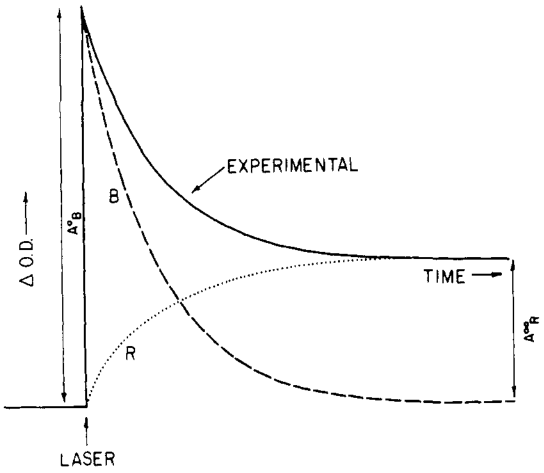
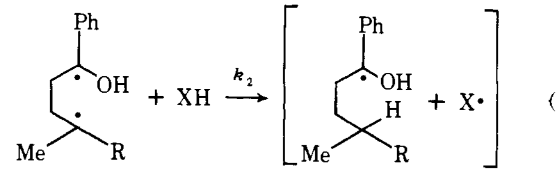


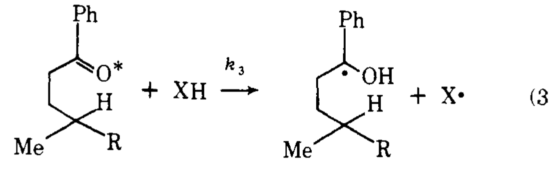
Figure 1. Calculated trace (solid line) resulting from the addition of transient absorbances due to the biradical (dashed trace) and the free radical (dotted line).

The samples were irradiated with the pulses (337.1 nm, 8 ns, 3 mJ) from a nitrogen laser, and the resulting transient absorptions, reflecting the presence of ketyl radical centers, were monitored using a detection system with nanosecond response. In the presence of a hydrogen donor, XH, reaction 2 takes place. The same products can also be produced in a process involving hydrogen abstraction by the triplet state, reaction 3.



(2)

B 3



(3)

3

Reaction 3 does not interfere with the kinetic analysis (see below), unless so many triplets are trapped by XH that biradical input becomes too low for the accurate determination of rate constants. This was the case in the valerophenone-tri-*n*-butylstannane system, for which we were unable to obtain reliable kinetic parameters. In the case of mercaptans Wagner et al. have shown that hydrogen abstraction by excited carbonyl compounds is so slow[11] that reaction 3 can in many cases be ignored.

In the type of experiments described in this paper one usually monitors the transient absorption due to the ketyl chromophore; the extinction coefficients for the biradical B and radical **3** are essentially identical.[7] When the reaction of interest destroys this chromophore, this approach is equivalent to monitoring directly the species of interest, i.e., the case for biradical decay in the absence of hydrogen donors. The example considered herein (reaction 2) is somewhat different: while hydrogen abstraction results in biradical consumption, it does not result in a decrease of the concentration of ketyl chromophores, which, in fact become longer lived as a result of the long lifetime of radical **3**. All our experiments indicate that **3** should be regarded as a stable species in the time scale of our experiments, suggesting that hydrogen abstraction by **3** is considerably slower than by the alkyl site in B.

The transient kinetics for this system correspond to a combination of parallel first-order growth (radical) and decay (biradical) processes. The kinetics of the latter is given by

$$d[B]/dt = -k_{expt}[B] \tag{4}$$

where

$$k_{expt} = k_B + k_2[XH] \tag{5}$$

and k_B is the reciprocal of the biradical lifetime ($k_B = \tau_B^{-1}$).

In systems where $\tau_B > \tau_T$, as is the case here,[10] the kinetics of the reaction can be represented by very simple expressions. Equations 6a and 6b are the expressions for biradical decay in terms of concentration and optical density (A).

$$\ln([B]^0/[B]) = k_{expt}t \tag{6a}$$

$$\ln(A_B{}^0/A_B) = k_{expt}t \tag{6b}$$

For the radical **3** (indicated as R) the change of radical concentration is related to the variation in [B] by the equation

$$d[R] = -\frac{k_2[XH]}{k_{expt}}d[B] \tag{7}$$

Integrating leads to

$$[R] - [R]^0 = -\frac{k_2[XH]}{k_{expt}}\{[B] - [B]^0\} \tag{8}$$

and combining with eq 9a-c leads to eq 10.

$$[R]^0 \equiv 0 \tag{9a}$$

$$[B]^0 = [R]^\infty \frac{k_{expt}}{k_2[XH]} \tag{9b}$$

$$[B] = [B]^0 \exp(-k_{expt}t) \tag{9c}$$

$$\ln\left(\frac{[R]^\infty}{[R]^\infty - [R]}\right) = k_{expt}t \tag{10a}$$

$$\ln\left(\frac{A_R{}^\infty}{A_R{}^\infty - A_R}\right) = k_{expt}t \tag{10b}$$

Combining eq 6b and 10b leads to the kinetic expression

$$\ln\left(\frac{A - A_R{}^\infty}{A_B{}^0 - A_R{}^\infty}\right) = -k_{expt}t \tag{11}$$

Both differences in optical density in eq 11 [i.e., ($A - A_R{}^\infty$) and ($A_B{}^0 - A_R{}^\infty$)] can be measured directly from the experimental traces. In fact eq 11 is entirely equivalent to eq 6 if one allows the base line to move up to the experimental final level; see Figure 1. Figure 2 shows a typical plot according to eq 11 and (insert) the corresponding experimental trace. Typically, the data from 20-40 laser shots was averaged to obtain each trace. The bimolecular rate constants for hydrogen abstraction can be derived from a plot of ($k_{expt} - \tau_B{}^{-1}$) vs. [XH], Figure 3 (τ_B = 76 ns). The corresponding values are summarized in Table I.

As pointed out above, reaction 3 can be of importance in the case of tri-*n*-butylstannane.[3] The generation of ketyl radicals (and therefore transient absorptions) in this reaction is mathematically equivalent to a vertical displacement of the decay trace of Figure 1 and does not affect the treatment of the data, though in some cases the occurrence of reaction 3 can make the values of $A_R{}^\infty$ rather close to the initial optical density, therefore making the study of the decay traces difficult; such is the case for the valerophenone-Bu_3SnH system, for which we were unable to obtain a reliable value of k_2.

In the case of Bu_3SnH, reaction 3 leads to optical absorptions due not only to ketyl radicals, but also to Bu_3Sn• radicals. While these signals do not affect the kinetics, they result in a

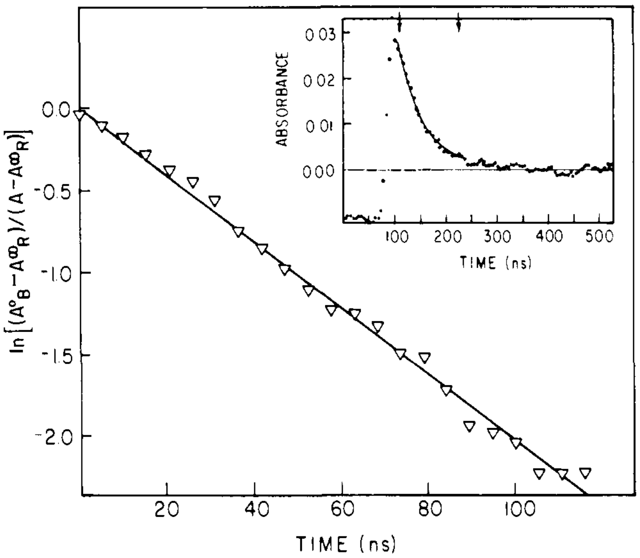


Figure 2. Kinetic plot according to eq 11 for γ-methylvalerophenone biradicals reacting with octanethiol (0.625 M). Insert: corresponding decay trace; the arrows indicate the section of decay used to determine the experimental rate constant.

vertical shift of the decay traces and the experimental values for $\mathcal{A}^\infty$ cannot be attributed solely to ketyl radicals.

Discussion

The lifetimes of the biradicals produced in the Norrish type II reaction of phenyl alkyl ketones have been the subject of studies by competitive methods,[3,5] as well as by flash techniques.[6,7,13,14] The reported values for those lifetimes are around 1 μs by competitive techniques[3] and 100 ns from time resolved experiments.[6,7] The results reported in this paper, and shown in Table I, show that the discrepancy simply reflects the uncertainty in the rate constants for hydrogen abstraction from thiols.[12] Indeed, the $k_2\tau_B$ value obtained from the flash experiments is within a factor of 2 of the Stern-Volmer slope ($k_2\tau_B$ = 1.8 M^{-1}) obtained in the competitive experiments.[3] Considering the entirely different nature of the two experiments, the agreement may be regarded as excellent.

The rate constant for the reaction of the biradical from γ-methylvalerophenone with tri-*n*-butylstannane (1.1 × 10^6 M^{-1} s^{-1}) is in excellent agreement with the value reported by Carlsson and Ingold for the reaction of *tert*-butyl radicals with the same substrate (7.4 × 10^5 M^{-1} s^{-1}).[15] Such an agreement confirms that radical centers in biradicals react in hydrogen-transfer reactions with the same rate constants as monoradicals with the same substitution at the radical center. Application of this conclusion to the data for mercaptans indicates that secondary and tertiary alkyl radicals will also react with rate constants in the neighborhood of 10^7 M^{-1} s^{-1}.[16] Values reported earlier have ranged from 10^5 to 10^8 M^{-1} s^{-1}.[12] It is interesting to note that the determination of some rate constants for radical sites may be considerably easier using biradicals rather than monoradicals, because the former decay via clean first-order processes; this is the case for mercaptans and also for a wide range of electron acceptors.[6]

The value of the quantum yield of biradical trapping, Φ_T, and the experimental absorbances, $\mathcal{A}_R^\infty$ and $\mathcal{A}_B^0$, are related by the equation

$$\Phi_T = \frac{\mathcal{A}_R^\infty}{\mathcal{A}_B^0}\frac{\epsilon_B}{\epsilon_R f} \qquad (12)$$

where f is the fraction of free radicals that escape from the solvent cage and ϵ_B and ϵ_R are extinction coefficients. The values of $\mathcal{A}_B^0/\mathcal{A}_R^\infty$ are expected to follow a Stern-Volmer type of behavior:

$$\frac{\mathcal{A}_B^0}{\mathcal{A}_B^\infty} = \frac{\epsilon_B}{\epsilon_R f}\left(1 + \frac{1}{k_2\tau_B[XH]}\right) \qquad (13)$$

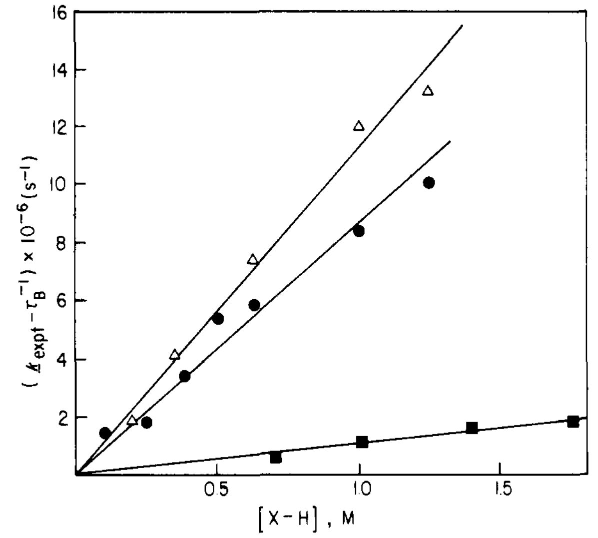


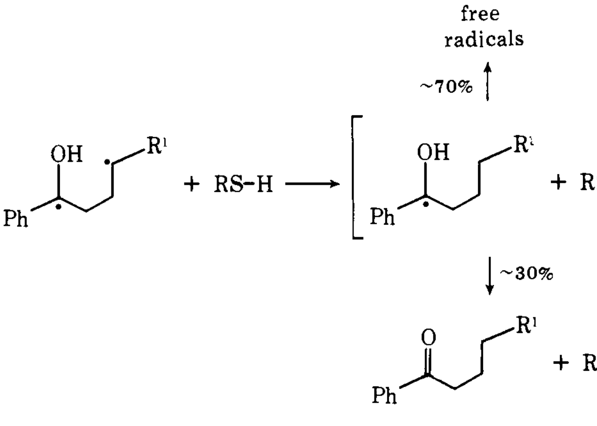
Figure 3. Plots according to eq 5 for valerophenone-octanethiol (Δ), γ-methylvalerophenone-octanethiol (●), and γ-methylvalerophenone-Bu$_3$SnH (■). The solvent is 1.2 M pyridine in benzene, the temperature is 22 °C, and τ_B = 76 ns.

Table I. Rates of Hydrogen Abstraction by Type II Biradicals[a]

ketone	H donor	k_2/M^{-1} s^{-1}
γ-methylvalerophenone	Bu$_3$SnH	1.1 × 10^6
γ-methylvalerophenone	*n*-(C$_8$H$_{17}$)SH	9 × 10^6
valerophenone	*n*-(C$_8$H$_{17}$)SH	11.3 × 10^6

[a] At 22 °C in 1.2 M pyridine in benzene; the value of τ_B in this solvent is 76 ns, and within experimental error the same for both ketones.

Equation 13 is valid only when the quantum yield of intersystem crossing is one and under conditions where reaction 3 is not important. Figure 4 shows a plot of the data for the γ-methylvalerophenone-octanethiol system. From the intercept-to-slope ratio we obtain $k_2\tau_B$ = 0.50 M^{-1}, which compares well with the value of 0.68 M^{-1} which can be obtained as the product of the two values in Table I. The intercept in Figure 4 is 1.5, and a similar plot for valerophenone yields an intercept of 1.3. It seems clear that either $\epsilon_B > \epsilon_R$, which seems unexpected in view of earlier results,[7] or, more likely $f < 1$; that is, a considerable fraction of the radicals produced in reaction 2 undergo cage recombination ($f \sim 0.7$). The original trapping experiments in fact suggested that 1/3 of the ketyl and thiyl radicals disproportionate (or couple) in the cage.[3] The 30% cage reaction (14) for a pair of triplet-derived radicals is un-



(14)

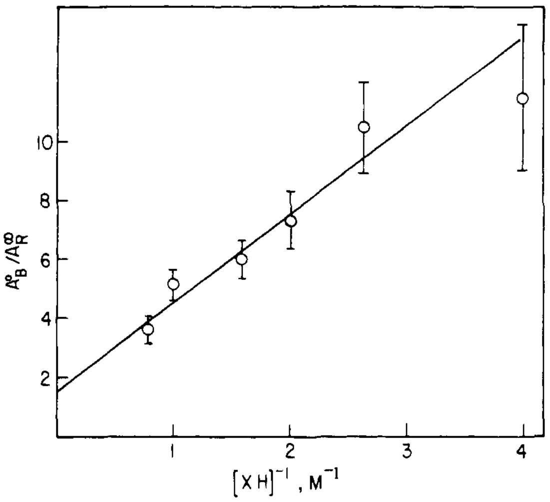


Figure 4. Plot according to eq 13 for γ-methylvalerophenone biradicals reacting with octanethiol.

usually high and may reflect the significant spin-orbit coupling in species with free spin on sulfur.[17]

Finally, Wagner et al.[3] failed to detect any biradical trapping in the valerophenone-Bu_3SnH system and attributed the result to the high efficiency of hydrogen abstraction by the triplet state. Our results confirm that k_2 is low enough to make the experiment extremely difficult in that system. γ-Methylvalerophenone (see Table I) has a considerably shorter triplet lifetime and minimizes the interference from reaction 3.

Experimental Section

Materials. γ-Methylvalerophenone (Fluka) and valerophenone (Aldrich) were distilled prior to use. Octanethiol was an Aldrich product and was vacuum distilled. Tri-*n*-butylstannane (K&K) was used as received. All experiments were carried out in 1.2 M pyridine in benzene.

Samples. They were contained in rectangular Suprasil cells with an optical path of 3 mm. The samples (1 mL) were deaerated by bubbling oxygen-free argon; in the case of samples containing Bu_3SnH, it was injected into already deaerated tubes in a glovebox filled with nitrogen.

Laser Flash Photolysis. The instrument makes use of a Molectron UV-400 nitrogen laser for excitation. A pulsed xenon lamp, combined with a B&L high-intensity monochromator, serves as a monitoring system. The signals from an RCA-4840 photomultiplier tube were terminated into 93 Ω and into a Tektronix R7912 transient digitizer; this unit was interphased with a PDP11/55 computer that controlled the experiment and processed the data. Typically 20-40 laser pulses were averaged to produce each experimental trace. Further details will be given elsewhere.[18]

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