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REACTION OF TRIETHYLSILYL RADICAL WITH SULFIDES, A LASER FLASH PHOTOLYSIS STUDY

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ABSTRACT

Triethylsilyl radical was generated by laser flash photolysis of a 1:1 (v/v) solution of triethylsilane and di-*tert*-butyl peroxide. The silicon centered radical was reacted with sulfides to give carbon centered radicals by displacement at sulfur. The carbon radicals were readily detected by their transient absorption spectra. The absolute rate of reaction of triethylsilyl radical with 9-fluorenylphenylsulfide, di-*n*-butylsulfide, di-*sec*-butyl sulfide, di-*tert*-butyl sulfide and di-*n*-butyl disulfide are $2{\cdot}40 \pm 0{\cdot}12 \times 10^8$ $\text{M}^{-1}\text{s}^{-1}$, $1{\cdot}1 \times 10^7 \pm 0{\cdot}89 \times 10^6 \text{M}^{-1}\text{s}^{-1}$, $8{\cdot}79 \pm 0{\cdot}73 \times 10^6$ $\text{M}^{-1}\text{s}^{-1}$, $3{\cdot}29 \pm 0{\cdot}18 \times 10^6$ $\text{M}^{-1}\text{s}^{-1}$, and $3{\cdot}41 \pm 0{\cdot}09 \times 10^8$ $\text{M}^{-1}\text{s}^{-1}$, respectively.

INTRODUCTION

Silicon and tin centered radicals rapidly abstract halogen atoms from alkyl halides to generate carbon centered radicals.[1] This approach has been used numerous times to generate organic radicals for study by electron paramagnetic resonance (EPR) or laser flash photolysis, or for use in organic synthesis. One of the more common approaches is to photolyze a solution of di-*tert*-butyl peroxide (DTBP) and triethylsilane containing a halogen atom donor RX. Under these conditions R· can be generated via reactions (1)–(3)

$$(tert\text{-BuO})_2 \xrightarrow{h\nu} 2\ tert\text{-BuO} \tag{1}$$

$$tert\text{-BuO}\cdot + \text{Et}_3\text{SiH} \longrightarrow tert\text{-BuOH} + \underset{\mathbf{1}}{\text{Et}_3\text{Si}\cdot} \tag{2}$$

$$\text{Et}_3\text{Si}\cdot + \text{RX} \longrightarrow \text{Et}_3\text{SiX} + \text{R}\cdot \tag{3}$$

In certain cases, halides are inconvenient precursors to free radicals, particularly when RX is too labile to isolate or it reacts on mixing with triethylsilane. Hart has encountered this problem in his synthetic work on free radical cyclizations and found that aryl sulfides are convenient substitutes for RX that are easily prepared and handled.[2] Although there are several absolute rate constants reported for reaction of **1** with halogen donors[3] no such data have been reported for sulfides. This has prompted our study of the absolute reactivity of triethylsilyl with various sulfides. This will allow a comparison of the reactivity of triethylsilyl with sulfides and the more traditionally used halide substrates.

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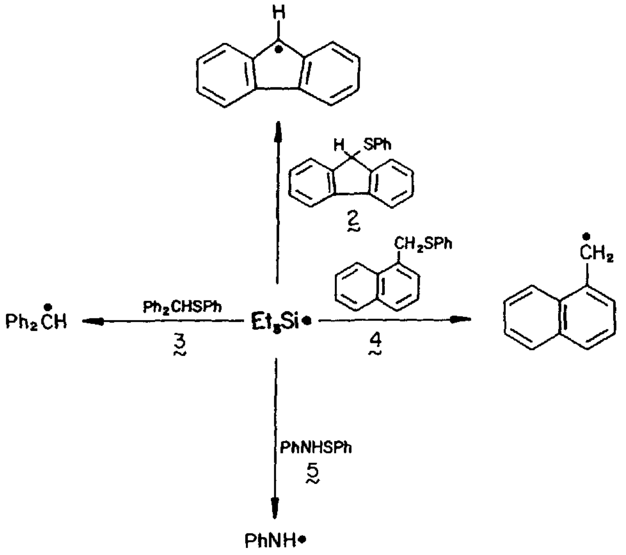
RESULTS AND DISCUSSION

Laser flash photolysis (337·1 nm) of 1/1 triethylsilane/DTBP (v/v) containing 9-fluorenylphenylsulfide **2** gives the transient absorption spectrum of Figure 1. This spectrum is identical to that of the 9-fluorenyl radical (FlH·) reported elsewhere.[4] In a similar fashion, flash photolysis of 1/1 triethylsilane/DTBP containing **3**, **4**, and **5** gave the transient spectra (Figures 2–4) of the benzhydryl, 1-naphthylmethyl and anilino radicals respectively. The spectra are in good agreement with those previously reported.[5–7] The organic radicals are produced by the sequence shown below.



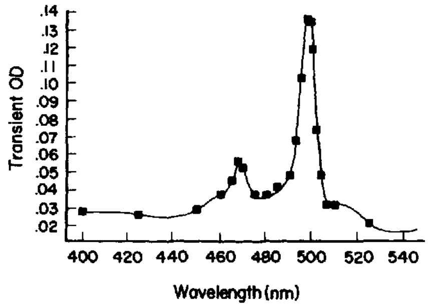


Figure 1. The transient absorption spectrum of 9-fluorenyl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing 9-fluorenylphenylsulphide

Control experiments with **2–5** in benzene demonstrated that direct laser excitation of these compounds does not produce detectable transient absorbance of the corresponding radicals. The quantum yield for process (4) must be low, but is not necessarily zero. Any radical formed in this reaction would appear 'instantaneously' on these time scales and would not interfere with the kinetic analysis (*vide infra*).

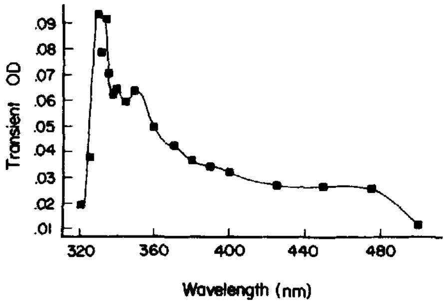


Figure 2. The transient absorption spectrum of benzhydryl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing **3**

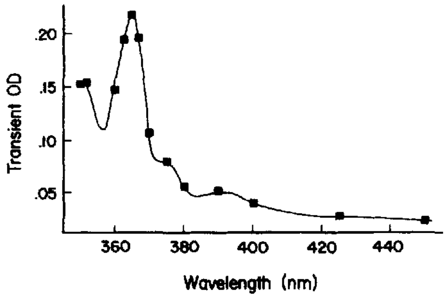
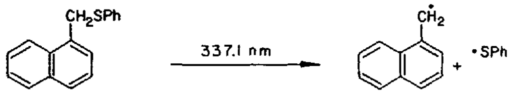


Figure 3. The transient absorption spectrum of 1-naphthylmethyl produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing **4**

Figure 4. The transient absorption spectrum of anilino radical produced by laser flash photolysis of 1/1 triethylsilane/DTBP containing **5**



(4)

The formation of 9-fluorenyl radical is not instantaneous (Figure 5). The formation of FlH follows first order kinetics to give k_{obs} according to (5)

$$\ln\left(\frac{A_\infty}{A_\infty - A_t}\right) = k_{\text{obs}}t \qquad (5)$$

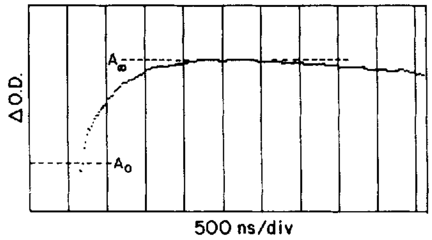
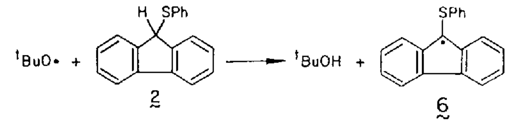


Figure 5. The formation of FlH· following laser flash photolysis of 1/1 triethylsilane/DTBP containing **2**

where A_∞ is the maximum in the transient absorption of FlH· following the laser pulse and A_t is the absorption at time = t. The value of A_∞ is taken at the plateau region of Figure 5 prior to the start of FlH· decay. Because the pseudo first order rate of formation of FlH is very much faster than its subsequent radical–radical decay, the two processes can be analyzed separately.[3]

There is no evidence for reaction of *tert*-butoxy radical with **2** as per equation (6) to give **6** under the conditions employed in this work.

 (6)

The spectra of radicals such as **6** are quite different from those of the corresponding hydrocarbon radicals and are quite easy to detect by flash photolysis.[8] We have generated **6** by photolysing solutions of **2** in DTBP alone (Figure 6), and this radical shows a λ_{max} at 490 nm, which is well separated from the sharp 500 nm maximum found for FlH·, but similar to the 490 nm λ_{max} reported for 9-chlorofluorenyl radical.[9] The complete absence of **6** under our conditions is not surprising. Scaiano has measured the absolute rate constant of reaction (2) to be $5{\cdot}7 \pm 0{\cdot}6 \times 10^6\ \text{M}^{-1}\text{s}^{-1}$ at 300K, thus the lifetime of *tert*-butoxy radical in the presence of

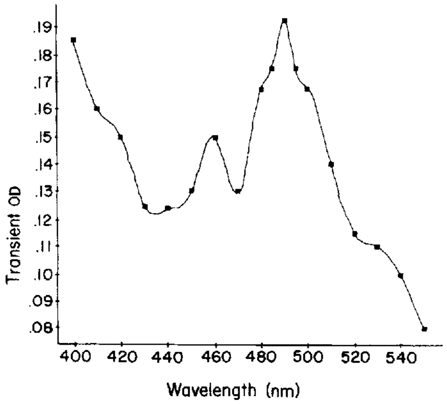


Figure 6. The transient absorption spectrum of 9-thiophenylfluorenyl radical, obtained by laser flash photolysis of DTBP containing 9-fluorenylphenylsulfide

3·13 M triethylsilane (1:1 Et_3SiH:DTBP) will be less than 56 ns.[4] Thus, even if the absolute rate constant of reaction (6) is as large as 10^7 $M^{-1}s^{-1}$, then the pseudo first order rate constant for the formation of **6** in a solution containing as much as 0·1 M **2** will be 18 times slower than the pseudo first order rate constant of formation of triethylsilyl radical. (Typical rate constants for H atom abstraction reactions of *tert*-butoxyl with ethers are ≈ $10^6 M^{-1}s^{-1}$.[10] The maximum concentration of **2** used in these experiments was 0·04 M thus we feel that 18 represents a conservative lower limit.) The observed pseudo first order rate constant for the formation of FlH· is related to k_q the absolute rate of reaction (5) by equation (7),

$$k_{obs} = k_o + k_q\,[\text{9-fluorenylphenylsulfide}] \tag{7}$$

where k_o represents all possible first order decay modes of triethylsilyl radical **1** in the absence of quencher. A plot of k_{obs} versus [**2**] from 0·005–0·04 M is linear. Two independent determinations of the quenching rate constant gave 2·40 ± 0·12 × 10^8 $M^{-1}s^{-1}$ and 2·58 ± 0·15 × 10^8 $M^{-1}s^{-1}$ (Figure 7). This rate constant is about 5 times slower than the rate constant for reaction of **1** with 9-bromofluorene (Table 1) which we have measured in this work.

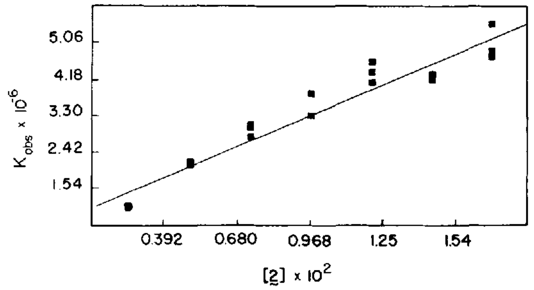


Figure 7. A plot of k_{obs} versus concentration of 9-fluorenylphenylsulfide obtained for its reaction with triethylsilyl (see text)

Table 1. The absolute rate constants of reaction of triethylsilyl radical with various quenchers

Reagent	$k_q(M^{-1}s^{-1})$	Footnote
9-bromofluorene	1·27 ± 0·13 × 10^9	a
9-fluorenylphenylsulfide	2·40 ± 0·12 × 10^8	a
n-Bu—S-*n*Bu	1·12 ± 0·89 × 10^7	a, b
sec-Bu—S-*sec*-Bu	8·79 ± 0·73 × 10^6	a, c
tert-Bu—S-*tert*-Bu	3·29 ± 0·18 × 10^6	a, d
n-Bu—S—S-*n*Bu	3·41 ± 0·09 × 10^8	a, e
n-Bu—Br[4]	5·4 ± 0·1 × 10^8	
tert-Bu—Br[4]	1·1 ± 0·5 × 10^9	
n-Bu—Cl[4]	3·1 ± 1·4 × 10^5	
tert-Bu—Cl[4]	2·5 ± 0·2 × 10^6	

a) This work, ± one standard deviation
b) Concentration range of quencher is 0·056–0·521 M
c) Concentration range of quencher is 0·071–0·521 M
d) Concentration range of quencher is 0·028–0·506 M
e) Concentration range of quencher is 0·0052–0·0392 M

The reaction of **1** with dialkyl sulfides (reaction 8) gives alkyl radicals which lack a suitable chromophore to allow for their direct detection by laser flash photolysis.

$$\mathrm{Et_3Si} + tert\text{-}\mathrm{Bu\text{-}S\text{-}}tert\text{-}\mathrm{Bu} \dashrightarrow \mathrm{Et_3SiS\text{-}}tert\text{-}\mathrm{Bu} + tert\text{-}\mathrm{Bu}. \tag{8}$$

The kinetics of these processes were monitored using a Stern–Volmer approach and 9-fluorenylphenyl sulfide as a probe.[3] In this experiment, the yield of FlH· (formed by flash photolysis of $\mathrm{Et_3SiH/DTBP}$) containing constant [**2**], was monitored as a function of added alkyl sulfide or disulfide. Under these conditions equation (9) holds

$$\frac{\phi^\circ}{\phi} = 1 + k_q\tau[\mathrm{q}] \tag{9}$$

where ϕ and ϕ° are the yields of FlH· in the presence and absence of alkyl sulfide respectively, k_q is the absolute rate constant of reaction (8), [q] is the concentration of alkyl sulfide quencher, and τ is the lifetime for the formation of triethylsilyl radical in the absence of sulfide quencher. The values of ϕ and ϕ° obtained by measuring $A_\infty - A_0$ as a function of quencher (Figure 5). Typical values of τ are in the range of 250–300 ns when [**2**] = 0·02 M. The quenchers do not absorb significantly at 337 (ε_{337} = 0·7 for di-*n*-butylsulfide and ε_{337} = 2·8 for di-*n*-butyl disulfide) thus quenching of the probe signal of FlH due to screening by the quencher is not a concern. Furthermore the observed rate constant of formation of FlH increases with quencher concentration, in accord with our mechanism. A typical plot of ϕ°/ϕ versus di-*n*-butyldisulfide is given in Figure 8, and values of k_q are listed in Table 1. The reactivity trend for triethysilyl radical is

Bu-S-Bu > *sec*-Bu-S-sec-Bu > *tert*-Bu-S-*tert*-Bu

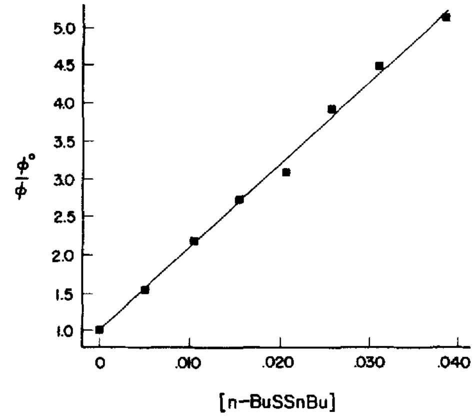


Figure 8. A plot of ϕ°/ϕ versus di-*n*-butyldisulfide, see text

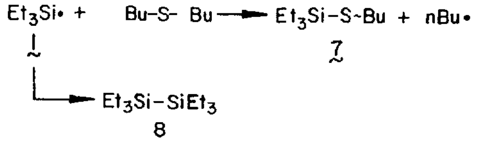
This trend is opposite to that of organic radical stability (primary < secondary < tertiary). Obviously a steric interaction must offset the effect of radical stability. The spread in rate constants in this series is only 3–4 which indicates that the transition structure for reaction (8) is very early and involves more S—Si bond making than C—S bond breaking. The absolute reactivity of triethylsilyl radicals with alkylsulfides is comparable to the rate of reaction of **1** with chlorides and much slower than the reaction of **1** with bromides or iodides.

Di-*n*-butyl disulfide reacts nearly 100 times more rapidly with **1** than do the dialkyl sulfides.

$$\mathrm{Et_3Si} + \text{Bu-S-S-Bu} \rightarrow \mathrm{Et_3Si}\text{-}n\text{-Bu} + n\text{-BuS}\cdot \qquad (10)$$

This is a consequence of the relatively low bond dissociation energy of C—S (rather than S—S) in a disulfide (52·6–56·6 versus 74 kcal/mol).[11] The longer bond length of S—S relative to C—S (2·05 versus 1·82Å)[11] may also lead to increased steric accessibility of the disulfide sulfur, which will accelerate the rate of homolytic displacement.

Chemical analysis of the DTBP, triethylsilane, di-*n*-butylsulfide system support the proposed mechanism. Photolysis of 0·1 M dibutylsulfide and 0·1 M DTBP in triethylsilane gives a high yield (79%) of silyl sulfide **7** as required by the proposed mechanism. A small quantity of hexaethyldisilane **8** was also formed in the reaction. It was not possible to perform product studies of this type using benzylic sulfides due to the light sensitivity of both the reactants and of the expected reaction products.



CONCLUSIONS

The absolute rate constants for reactions of triethylsilyl radical with various sulfides can be readily monitored by laser flash photolysis. They are similar to those for the corresponding alkyl chlorides and much slower than those for the corresponding bromides. This implies that sulfides can be used as convenient precursors for radical generation when the corresponding halide is inconvenient. The kinetics of the reaction are more sensitive to steric effects than to the stability of the radical reaction product which implies a transition state with more sulfur-silicon bond making than carbon-sulfur bond breaking.

EXPERIMENTAL

Triethylsilane (Aldrich) and DTBP (Mallinkrodt) were used as received. Solutions were placed in 1 cm^2 suprasil quartz cells and deoxygenated by bubbling with high purity nitrogen. The samples were irradiated with the pulses of a Molectron UV-22 Nitrogen laser (337·1 nm, 6 mJ, 10 ns) which were passed through a beam splitting prism to be coincident with a 1000 Watt xenon arc lamp monitoring beam. In some cases a Lumonics TE-861-4 Excimer laser using a Xe, F_2, He gas mix (350 nm, ~80 mJ, 10 ns) was used as the excitation source. Suitable Ealing glass filters were placed between the sample and monochromator photomultiplier tube assembly to prevent laser radiation from impinging on the detector. The monitoring beam was focused on the slit of an Oriel Monochrometer with approximately 1 mm front and rear slits. Signals were obtained with an IP 28 photomultiplier tube detector (4 ns response time) and were digitized by a Tektronix 7912 A/D converter. The experiment was controlled by an Apple IIe microcomputer which was also used for storage, processing, and hard copies of the data. Absorption spectra were obtained from flowed solutions. Kinetic studies were performed using static samples.

9-Fluorenylphenylsulfide (**2**), diphenylmethylphenylsulfide (**3**), 1-naphthyl methylphenylsulfide (**4**) and N-phenylbenzene-sulfenamide used in this study were prepared and purified by procedures described in the literature.[12–15]

Product analyses were performed by photolyzing degassed solutions sealed in pyrex tubes with a Rayonet Reactor using RPR-350 light sources. The products were analyzed on a Hewlett Packard 5830A G. C. using a 6 ft by 1/8″ SE-30 column.

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