University Chem. Labs, Cambridge, for converting it into $Os_3(CO)_{12}$ for us. NMR studies were supported by Grant No. CHE-7916210 from the National Science Foundation. We wish to thank the reviewers for their thoughtful comments.

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Supplementary Material Available: Listings of structure factor amplitudes for both crystallographic analyses (30 pages). Ordering information is given on any current masthead page.

Absolute Rate Constants for the Reactions of *tert*-Butoxyl Radicals and Some Ketone Triplets with Silanes[1]

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Absolute rate constants for the reactions of *tert*-butoxyl radicals and some ketone triplets with a variety of silanes have been measured by a laser flash technique. At 300 K rate constants, k_a, for H atom abstraction by *tert*-butoxyl from, e.g., Et_3SiH, n-$C_5H_{11}SiH_3$, $C_6H_5SiH_3$, and Cl_3SiH are 5.7, 10.6, 7.5, and $\sim 40 \times 10^6$ M^{-1} s^{-1}, respectively, and for quenching the benzophenone triplet, 9.6, 8.8, 5.0, and $\sim 7.6 \times 10^6$ M^{-1} s^{-1}, respectively, the principal reaction in all these cases being abstraction of an H atom bound to silicon. With $(EtO)_3SiH$, however, *tert*-butoxyl abstracts hydrogen, $k_a = 2.0 \times 10^6$ M^{-1} s^{-1}, from the methylene positions rather than from the silicon. The effect (or lack of it) produced by neighboring phenyl, alkoxy, and chlorine substituents on the ease of formation of silyl radicals is discussed in relation to formation of the analogous carbon-centered radicals. Additional kinetic data are presented together with the UV absorption spectra of some silicon-centered radicals.

Silanes which contain silicon-hydrogen bonds are known to react with a variety of free-radicals to form silyl radicals.[3,4] Although these are important intermediates in many chemical reactions, absolute rate data regarding their formation from silanes are extremely limited.[5,6] Utilizing the techniques of kinetic EPR spectroscopy and laser flash photolysis, we have recently embarked upon a research program which will provide a reliable body of quantitative kinetic data for many of the important reactions of group 4 centered organometallic radicals in solution.[7,8] For such studies, the preferred method for generating the organometallic radical is hydrogen atom abstraction from an appropriate precursor in a very fast (essentially "instantaneous") photoinitiated process. The preferred hydrogen atom abstracting agents will be *tert*-butoxyl radicals or ketone triplets. Although the *tert*-butoxyl/silane reaction has been very extensively used for silyl radical generation,[9] only for triethylsilane has a rate constant been measured (6×10^6 M^{-1} s^{-1} at 300 K, as reported in our preliminary communication).[7] For ketone triplets the literature contains one report indicating that the reaction does take place when ketone/organosilane systems are examined by EPR spectroscopy,[10] plus a gas-phase study of the acetone/SiH_4 system.[11] In addition, a semiempirical calculation based on the bond energy bond order (BEBO) method predicted that the photoreduction of benzophenone triplets by trimethylsilane should occur with a rate constant of 3×10^6 M^{-1} s^{-1} at 298 K and an activation energy of 3.05 kcal/mol.[12]

Experimental Section

Materials. All the reagents and solvents used in this work were commercial materials which were purified by standard methods before use.

Procedure. The experiments were carried out under oxygen-free conditions using the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV 24 nitrogen laser for excitation. The experimental system has been interfaced with a PDP-11/03L computer that controls the experiment and provides suitable data gathering, storage, and hardcopy facilities. Complete details have been given elsewhere.[13]

Results

Reactions with *tert*-Butoxyl Radicals. The rates of reaction of *tert*-butoxyl radicals with various silanes were measured by using the technique described previously,[14]

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[1] Issued as N.R.C.C. No. 19985.

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[3] For a concise general review, see: Sakurai, H. *Free Radicals* **1973**, *2*, 741–808.

[4] For a comprehensive review of kinetic data for hydrogen abstraction from silanes in the gas phase, see: Arthur, N. L.; Bell, T. N. *Rev. Chem. Intermed.* **1978**, *2*, 37–74.

[5] The gas phase data are restricted to abstractions by atoms and carbon-centered radicals[4] while the liquid-phase data are restricted to carbon-centered radicals.[6]

[6] See, e.g.: Aloni, R.; Rajbenbach, L. A.; Horowitz, A. *Int. J. Chem. Kin.* **1981**, *13*, 23–38.

[7] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C.; Woynar, H. *J. Am. Chem. Soc.* **1981**, *103*, 3231–3232.

[8] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.*, in press.

[9] See, e.g. (a) Sakurai, H.; Hosomi, A., Kumada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1551. (b) Hudson, A.; Jackson, R. A. *J. Chem. Soc. D* **1969**, 1323–1324. (c) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 3938–3940. (d) Frangopol, P. T.; Ingold, K. U. *J. Organomet. Chem.* **1970**, *25*, C9–C12. (e) Bowles, A. J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc. B* **1971**, 1947–1949.

[10] Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1933–1937.

[11] O'Neal, H. E.; Pavlou, S.; Lubin, T.; Ring, M. A.; Batt, L. *J. Phys. Chem.* **1971**, *75*, 3945–3949.

[12] Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 934–938.

[13] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.

[14] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

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Table I. Representative Kinetic Data for the Reaction of *tert*-Butoxyl and Benzophenone Triplets with Triethylsilane at 302 K[a]

reagent	$[(CH_3CH_2)_3SiH]$/M	k_{exptl} or k_d/s^{-1}
$(CH_3)_3CO·$	0	1.30×10^6
	0.031	1.50×10^6
	0.093	1.90×10^6
	0.154	2.18×10^6
	0.242	2.85×10^6
	0.242	2.68×10^6
$(C_6H_5)_2CO^*$	0.032	7.0×10^5
	0.062	1.08×10^6
	0.124	1.59×10^6
	0.183	2.06×10^6
	0.242	2.75×10^6

[a] For complete details see Tables IV and V of the supplementary material.

Table II. Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Some Silanes and Other Compounds at 300 K

substrate	k_a/M^{-1} s^{-1} [a]	ref
$(CH_3CH_2)_3SiH$	$(5.7 \pm 0.6) \times 10^6$ [b]	this work
n-$C_5H_{11}SiH_3$	$(1.06 \pm 0.08) \times 10^7$	this work
$C_6H_5SiH_3$	$(7.5 \pm 1.3) \times 10^6$	this work
$C_6H_5Si(CH_3)_2H$	$(6.6 \pm 1.0) \times 10^6$	this work
$(CH_3CH_2O)_3SiH$	$(2.0 \pm 0.3) \times 10^6$	this work
$(CH_3CH_2)_4Si$	$(1.2 \pm 0.4) \times 10^6$	this work
Cl_3SiH	$(4.0 \pm 3.0) \times 10^7$ [c]	this work
$C_6H_5CH_3$	2.3 ± 10^5 [d]	14
$C_6H_5C(CH_3)_2H$	8.7 ± 10^6 [d]	14
Cl_3CH	$(4.55 \pm 0.23) \times 10^5$	this work
$(C_2H_5)_2O$	3.9×10^6	15
$(n$-$C_4H_9)_3SnH$	1.9×10^8 [b]	16

[a] Error limits represent 95% confidence level. [b] Value derived from the complete kinetic study between 253 and 345 K, not just from the data at this temperature. [c] See text. [d] At 295 K.

in which diphenylmethanol is used as a probe and the photolysis of di-*tert*-butyl peroxide as the *tert*-butoxyl source.

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO· \qquad (1)$$

$$Me_3CO· + RR'R''SiH \rightarrow Me_3COH + RR'R''Si· \qquad (2)$$

$$Me_3CO· + Ph_2CHOH \xrightarrow{k_B} Me_3COH + Ph_2\dot{C}OH \qquad (3)$$

In this technique, the kinetics of the formation of $Ph_2\dot{C}OH$ are monitored for a series of samples with a constant concentration of diphenylmethanol and variable concentrations of substrate. The time profiles for the formation of $Ph_2\dot{C}OH$ (montored at 540 nm) lead to an experimental pseudo-first-order rate constant,[14] k_{exptl}, which is related to the elementary steps of interest according to eq 4, where

$$k_{exptl} = k_0 + k_B[Ph_2CHOH] + k_a[substrate] \qquad (4)$$

k_0 is the rate of *tert*-butoxyl decay in the solvent (controlled by hydrogen abstraction and β scission) and k_a and k_B the rate constants for the reactions of *tert*-butoxyl with the substrate and diphenylmethanol, respectively. Since the concentration of the latter is a constant, eq 4 reduces to eq 5.

$$k_{exptl} = k_0' + k_a[substrate] \qquad (5)$$

The values of k_a obtained in this way are absolute rate constants and measure the overall (or molecular) reactivity of the substrate, regardless of the site or mechanism of reaction. The solvent used in these experiments was a 1:2 (v/v) mixture of benzene/di-*tert*-butyl peroxide. Table I shows representative values of k_{exptl} for triethylsilane from which the value of k_a at 300 K can be obtained. The results are summarized in Table II together with data for a few representative substrates which had been measured previously.[14-16]

The measurements with Cl_3SiH were particularly difficult, and the reproducibility was significantly less than in other experiments. It seems likely that the problem was caused by hydrolysis by traces of water. The errors given are the result of the comparison of five independent series of experiments. Competitive experiments in which *tert*-butoxyl radicals generated from the corresponding hyponitrite were made to compete for a mixture of $(C_2H_5)_3SiH$ and Cl_3SiH (monitored by NMR), confirmed the substantially higher reactivity of the latter. No supplementary material is provided for this substrate.

For triethylsilane the temperature dependence for reaction with *tert*-butoxyl was examined in 1:2 (v/v) benzene/di-*tert*-butyl peroxide. Between 253 and 345 K the results could be represented by

$$\log (k_a/M^{-1}\ s^{-1})^{(C_2H_5)_3SiH}_{Me_3CO·} = (8.69 \pm 0.46) - (2.64 \pm 0.62)/\theta$$

where $\theta = 2.3RT$ kcal/mol and the errors correspond to 95% confidence limits.

Reactions with Carbonyl Triplets. As is frequently the case,[17-20] carbonyl triplets, particularly the benzophenone triplet, react in much the same manner and at a similar rate to *tert*-butoxyl radicals, e.g.

$$Ph_2CO^* + RR'R''SiH \rightarrow Ph_2\dot{C}OH + RR'R''Si· \qquad (6)$$

The silyl radicals generated in this reaction may add to the parent carbonyl compound,[7,10] e.g.

$$RR'R''Si· + Ph_2CO \rightarrow RR'R''SiO\dot{C}Ph_2 \qquad (7)$$

Reaction 7 and analogous processes will be the subject of a comprehensive kinetic study to be reported elsewhere. For the present purpose our aim was merely to minimize the interference of this reaction with the measurement of the kinetics of reaction 6. To achieve this, work was carried out at relatively low ketone concentrations and in solvents that could act as silyl radical scavengers such as benzene[21] and carbon tetrachloride.[3] However, it should be added that the rate constants which were measured are for triplet quenching. That is, if in addition to hydrogen abstraction (reaction 6) any other mode of quenching were involved, then this other process would be included in the measured rate constant. In these experiments the T–T absorptions were monitored at or near one of the absorption maxima (525 nm for benzophenone,[22] 645 nm for xanthone,[13] 486 nm for benzil,[23] and 390 nm for *p*-methoxyacetophenone[24,25]). The pseudo-first-order rate constants for

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[15] Malatesta, V.; Scaiano, J. C. *J. Org. Chem.*, submitted for publication.

[16] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399–5400.

[17] Padwa, A. *Tetrahedron Lett.* **1964**, 3465–3469.

[18] Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 3361–3364.

[19] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–177.

[20] Scaiano, J. C. *J. Photochem.* **1973/1974**, *2*, 81–118.

[21] Griller, D.; Marriot, P. R.; Nonhebel, D.; Perkins, M. J.; Wong, P. C. *J. Am. Chem. Soc.* **1981**, *103*, 7761.

[22] Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144–149.

[23] Porter, G.; Windsor, M. W. *Proc. R. Soc. London, Ser. A* **1958**, *A245*, 238–258.

[24] Selwyn, J. C.; Scaiano, J. C. *Polymer* **1980**, *21*, 1365–1366.

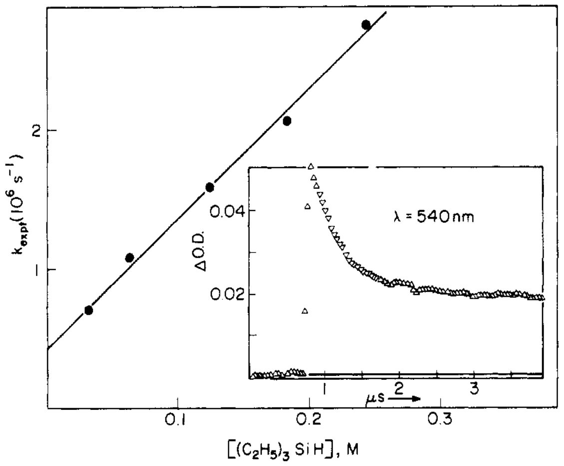

Figure 1. Quenching of benzophenone triplets by triethylsilane in benzene at 302 K, monitored at 525 nm. Insert: decay trace obtained at 540 nm (the residual optical density is proportional to the yield of ketyl radicals).

Table III. Rate Constants for the Quenching of Some Carbonyl Triplets by Some Organosilanes at 300 K

ketone	silane	solvent	k_r/M^{-1} s^{-1} [a]
benzophenone	$(CH_3CH_2)_3SiH$	C_6H_6	(9.6 ± 0.8) × 10^6
benzophenone	n-$C_5H_{11}SiH_3$	C_6H_6	(8.8 ± 1.2) × 10^6
benzophenone	$C_6H_5SiH_3$	C_6H_6	(5.0 ± 0.1) × 10^6
benzophenone	Cl_3SiH	C_6H_6	(7.6 ± 6.0) × 10^6 [b]
xanthone	$(CH_3CH_2)_3SiH$	CCl_4	(6.0 ± 1.0) × 10^7
benzil	$(CH_3CH_2)_3SiH$	C_8H_{18} [c]	<10^5 [d]
p-methoxyacetophenone	$(CH_3CH_2)_3SiH$	C_6H_6	~8 × 10^5 [d]

[a] Error limits represent 95% confidence level. [b] See text. [c] Isooctane. [d] No supplementary material.

triplet decay, k_d, were measured for several concentrations of the silane (see Table I), and the bimolecular rate constant, k_r, was determined from a plot of k_d vs. the silane concentration. Figure 1 illustrates a typical plot, the insert showing a trace of the evolution of the signal at 540 nm. Since the ketyl radical also has a strong absorption at 540 nm, some signal remains following the triplet decay. Values of k_r for several ketone/silane combinations are summarized in Table III. As in the case of *tert*-butoxyl, reproducibility was a problem with Cl_3SiH.

For the benzophenone/triethylsilane system the temperature dependence of the triplet quenching rates in benzene were measured between 280 and 345 K and could be represented by

$$\log\,(k_r/\mathrm{M^{-1}\,s^{-1}})_{Ph_2CO^*}^{(C_2H_5)_3SiH} = (8.89 \pm 0.24) - (2.61 \pm 0.34)/\theta$$

in excellent agreement with the results of the BEBO calculation[12] (vide supra). For this reaction the yield of ketyl radicals was estimated from the residual absorption at 540 nm (see insert in Figure 1).[26] That is, the ratio of optical densities after (ketyl) and before (triplet) decay is proportional to the yield of ketyl radicals. The reaction of benzophenone triplets with triethylamine was used as an actinometer.[27] At 300 K we estimate that ca. 85% (which may not be significantly different from 100%) of the quenching events led to the formation of a ketyl radical.[28] A similar study for $C_6H_5SiH_3$ leads to a value of 74% for the yield of ketyl radicals.

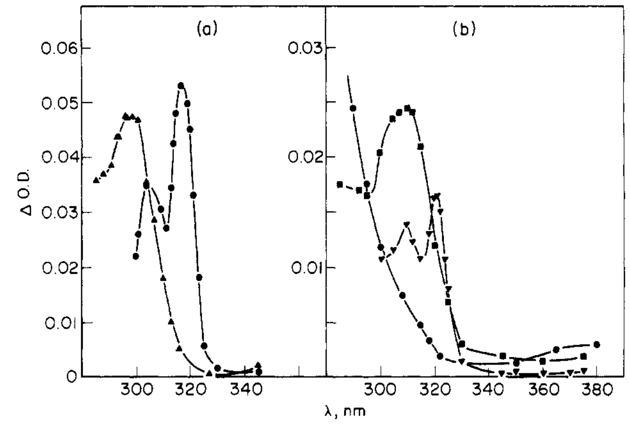

Figure 2. Comparison of transient absorption spectra for silicon- and carbon-centered radicals: $C_6H_5\dot{Si}H_2$ (▲, 2a), $C_6H_5\dot{C}H_2$ (●, 2a), $(C_2H_5)_3Si\cdot$ (●, 2b), $C_6H_5\dot{Si}(CH_3)_2$ (■, 2b) and $C_6H_5\dot{C}(CH_3)_2$ (▼, 2b), obtained at 300 K in di-*tert*-butyl peroxide/isooctane mixtures. The ratios of ΔOD are not a direct measure of the ratios of extinction coefficients for the corresponding transients because the samples were not matched and the sensitivity of the instrument varies on a day-to-day basis.

Absorption Spectra of Some Silyl Radicals. The reaction of *tert*-butoxyl radicals with the various silanes provided an excellent source of silyl radicals for spectroscopic study. Figure 2a shows the spectra recorded for $C_6H_5\dot{Si}H_2$ and $C_6H_5\dot{C}H_2$ (the last being in good agreement with the spectrum reported in the literature)[29] and Figure 2b the spectra for $(C_2H_5)_3\dot{Si}$, $C_6H_5\dot{Si}(CH_3)_2$, and $C_6H_5\dot{C}(CH_3)_2$.

Decay of Triethylsilyl Radicals. While all the triethylsilane experiments described above depend upon the detection of a species other than $(C_2H_5)_3Si\cdot$, this radical can be detected at sufficiently short wavelengths (see Figure 2). At the concentrations necessary for detection of these weak signals, their decay in isooctane/di-*tert*-butyl peroxide/triethylsilane (8:2:1) as solvent occurs with clean second-order kinetics and with $2k_t/\epsilon_{308\mathrm{nm}} = 1.1 \times 10^7$ cm^{-1} s^{-1} at 300 K.[30]

$$2(C_2H_5)_3Si\cdot \xrightarrow{2k_t} \text{products} \qquad (8)$$

In order to convert this value to an absolute rate constant, the transient optical absorption due to $(C_2H_5)_3Si\cdot$ at 308 nm was compared with that due to $Ph_2\dot{C}OH$ at 540 nm, both radicals being generated by hydrogen abstraction from the parent molecules with *tert*-butoxyl radicals. Taking ϵ_{540} for $Ph_2\dot{C}OH$ to be 3220 M^{-1} cm^{-1},[31] ϵ_{308} for $(C_2H_5)_3Si\cdot$ was estimated to be 1100 ± 600 M^{-1} cm^{-1}. The value of $2k_t$ is therefore ~1.2×10^{10} M^{-1} s^{-1} under these conditions, which indicates that triethylsilyl radicals decay at the diffusion-controlled limit, as do other sterically

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[25] Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154–4162.

[26] Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393–6397.

[27] Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048–1054.

[28] Spectral examination following triplet decay confirmed that the residual absorption was indeed due to $Ph_2\dot{C}OH$.

[29] Habersbergerová, A.; Janovský, I.; Teply, J. *Rad. Res. Rev.* **1968**, *1*, 109–181.

[30] This reaction probably yields both combination and disproportionation products. See: Tokach, S. K.; Koob, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 376–377; *J. Phys. Chem.* **1980**, *84*, 1–5. Cornett, B. J.; Choo, K. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1980**, *102*, 377–378. Gammie, L.; Safarik, I.; Strausz, O. P.; Roberge, R.; Sandorfy, C. *Ibid.* **1980**, *102*, 378–380.

[31] Land, E. J. *Proc. R. Soc. London, Ser. A* **1968**, *305*, 457–471.

unhindered group 4 centered radicals.[9d,32,33]

Discussion

Comparison of the kinetic data for the *tert*-butoxyl radicals (Table II) with that for the benzophenone n–π^* triplet (Table III) shows that these two species have a rather similar reactivity toward silanes—just as they do toward many other sustrates.[17-19] As is frequently the case,[13] xanthone was found to be more reactive than benzophenone, while benzil (due to its low triplet energy) and *p*-methoxyacetophenone (due to the π,π^* character of its triplet) are considerably less reactive.[34]

When trialkylsilanes and di-*tert*-butyl peroxide are photolyzed in the cavity of an EPR spectrometer, only trialkylsilyl radicals are observed.[3,9c,d,32] It was therefore not surprising to find that tetraethylsilane was significantly less reactive toward *tert*-butoxyl than triethylsilane. In fact, we estimate from the k_a values for these two silanes that about 80% of the attack occurs at the Si–H bond of triethylsilane. Similarly, for *n*-pentylsilane it seems probable that more than 80% of the reactivity is due to the SiH_3 group, the α-CH_2 group accounting for ca. 0.4×10^6 (i.e., 25% of the $(CH_3CH_2)_4Si$ k_a value) and the rest of the hydrocarbon chain for less than 1.0×10^6 M^{-1} s^{-1} of the measured k_a value.[35]

It is interesting to note that the reactivity of phenylsilanes toward *tert*-butoxyl radicals and benzophenone triplets is similar to that of alkylsilanes (cf. $C_6H_5SiH_3$ vs. n-$C_5H_{11}SiH_3$). For comparison, in the case of the carbon analogues, the CH_3 group in toluene is about 9 times more reactive than one of the CH_3 groups in 2,3-dimethylbutane.[36] We believe that the major cause of the lack of difference in the reactivities of phenylsilanes and alkylsilanes can be attributed to ineffective stabilization[33] of silicon-centered radicals by neighboring phenyl groups. In this connection, we note that the strong and well-resolved band observed for benzyl at 317 nm is shifted toward higher energies, viz., 297 nm for $C_6H_5SiH_2$ (see Figure 2a) and 306 nm for $C_6H_5\dot{S}i(CH_3)_2$ vs. 312 nm for $C_6H_5\dot{C}(CH_3)_2$. Moreover, this band is not as sharp or strong as that found for benzyl and related radicals. Furthermore, EPR spectroscopic studies of triarylsilyl radicals have shown that while there is some delocalization of spin into the aromatic rings[37-40] the extent of delocalization is less than for the corresponding triarylmethyl radicals.[39-42] No doubt reactivity differences between alkyl and arylsilanes would be enhanced if the attacking radical were less reactive, but even the trichloromethyl radical is remarkably unselective.[43]

Although a neighboring phenyl group fails to activate an Si–H bond toward reaction with *tert*-butoxyl, such activation is achieved with three neighboring chlorine atoms. This result was somewhat surprising because C–H bonds are not activated substantially by chlorine substitution; for example, chloroform and tertiary alkyl C–H bonds show similar reactivity toward *tert*-butoxyl (i.e., 4.55×10^5 and 2.7×10^5 M^{-1} s^{-1}, respectively).[45] This result is consistent with EPR studies which indicate that the $Cl_3Si\cdot$ radical is stabilized (with respect to $Cl_3C\cdot$, at least) by a bonding interaction between chlorine d orbitals and the semioccupied p orbital on the silicon, i.e., by $(d\text{-}3p)\pi$ bonding.[46] Polar factors must also play a role since trichlorosilane is about 1 order of magnitude less reactive than are trialkylsilanes toward $Cl_3C\cdot$ radicals.[43,44,47] It is also less reactive toward $CF_3\cdot$ radicals but is more reactive toward $CH_3\cdot$ radicals.[47]

Although a phenyl group has little effect and three chlorine atoms are activating, three ethoxy groups strongly deactivate a neighboring Si–H bond. In fact, EPR experiments with $(CH_3CH_2O)_3SiH$ showed that *tert*-butoxyl attack occurred predominantly at the CH_2 groups [$(CH_3CH_2O)_2Si(H)O\dot{C}HCH_3$, $a^H(1H) = 17.3$ and $a^H(3H) = 23.0$ G], no silicon-centered radical being detectable in the temperature range 165–297 K.[48] The low reactivity of this Si–H bond should probably be attributed to the electron-withdrawing effect of the three alkoxy substituents, which is not offset by any appreciable stabilization due to interactions of the unpaired electron with the p-type lone pairs on the oxygen atoms. The k_a value for diethyl ether (see Table II) also implies that triethoxysilane owes its reactivity to its ethoxy groups.

In conclusion, we note that the abstraction of hydrogen from most silanes by *tert*-butoxyl radicals and by some ketone triplets will be just fast enough to make silyl radical formation a sufficiently "instantaneous" process at high silane concentrations that time resolved studies of their further (secondary) reactions by laser flash photolysis are viable. We will report on the reactions of trialkylsilyl radicals with carbonyl compounds and organohalides elsewhere.

Registry No. $(CH_3CH_2)_3SiH$, 617-86-7; n-$C_5H_{11}SiH_3$, 10177-98-7; $C_6H_5SiH_3$, 694-53-1; $C_6H_5Si(CH_3)_2H$, 766-77-8; $(CH_3CH_2O)_3SiH$, 998-30-1; $(CH_3CH_2)_4Si$, 631-36-7; Cl_3SiH, 10025-78-2; Cl_3CH, 67-66-3; $(CH_3)_3CO\cdot$, 3141-58-0; $(C_6H_5)_2CO$, 119-61-9; $C_6H_5SiH_2$, 72975-30-5; $C_6H_5\dot{C}H_2$, 2154-56-5; $(C_2H_5)_3Si\cdot$, 24669-77-0; $C_6H_5\dot{S}i(CH_3)_2$, 32512-19-9; $C_6H_5\dot{C}(CH_3)_2$, 4794-07-4; xanthone, 90-47-1; benzil, 134-81-6; *p*-methoxyacetophenone, 100-06-1.

Supplementary Material Available: Tables of absolute rate constants for reactions of *tert*-butoxyl radical and some ketone triplets with silanes (19 pages). Ordering information is given on any current masthead page.

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(32) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 491–494. See also: Gaspar, P. P.; Haizlip, A. D.; Choo, K. Y. *Ibid.* **1972**, *94*, 9032–9037.

(33) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13–19.

(34) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614.

(35) Small, R. D., Jr.; Scaiano, J. C.; Patterson, L. K. *Photochem. Photobiol.* **1979**, *29*, 49–51.

(36) Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1515–1519.

(37) As judged by comparison of the ^{29}Si hyperfine splittings relative to those of trialkylsilyl radicals.[38,39]

(38) Geoffroy, M.; Lucken, E. A. C. *Helv. Chim. Acta* **1970**, *53*, 813–818.

(39) Gynane, M. J. S.; Lappert, M. F.; Riley, P. I.; Riviere, P.; Rivier-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5–12.

(40) Sakurai, H.; Umino, H.; Sugiyama, H. *J. Am. Chem. Soc.* **1980**, *102*, 6837–6840.

(41) As judged by comparison of the ring proton hyperfine splittings with those of the corresponding triarylmethyl radical.[40] The spin density on the central atom of Ar_3M radicals (Ar = 3,5-di-*tert*-butylphenyl) have been estimated to be 0.50 (M = C) and 0.78 (M = Si).[40]

(42) A similar conclusion was reached in an article published as the present paper was being considered for publication: Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252.

(43) For example,[44] relative rates for attack by $Cl_3C\cdot$ in refluxing CCl_4 for $Me(C_6H_{11})_2SiH$, $PhMe_2SiH$, Ph_2MeSiH, Ph_3SiH, and Cl_3SiH are 1.20:0.83:1.00:1.47:0.11, respectively.

(44) Sommer, L. H.; Ulland, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 3803–3806.

(45) See footnote 25 of ref 7.

(46) Lloyd, R. V.; Rogers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 2459–2464.

(47) Baruch, G.; Horowitz, A. *J. Phys. Chem.* **1980**, *84*, 2535–2539.

(48) It has previously been shown by EPR spectroscopy that in the reaction of *tert*-butoxyl radicals with $(CH_3CH_2O)_3CH$ the $(CH_3CH_2O)_2CHO\dot{C}HCH_3$ and $(CH_3CH_2O)_3C\cdot$ radicals are formed at approximately equal rates at 213 K.[49]

(49) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609–614.