J. Am. Chem. Soc. 1982, 104, 5119–5123

modes at 860 and 760 cm^{-1} flank this peak and are assigned to ν_{CC} modes. The spectra of di-*tert*-butyl peroxide contain three analogous bands.[24] The two ν_{CC} modes of lower symmetry, A_g and B_g, split from an E mode for a C_{3v} *tert*-butyl group, remain to be assigned as does the third infrared-active ν_{CC} mode (A_u or B_u species). Whether these *remaining* unassigned ν_{CC} modes couple with ρ_{CH_3} modes or not can be questioned. Coupling of triplet ρ_{CH_3} modes with ν_{CC} would be expected to break up the triplet pattern. One or two, but not all three bands of a triplet could couple with the A_g and B_g, ν_{CC}, modes. However, three or four sets of triplets are observed in the Raman spectrum with no obvious disruption.

Whether one applies such coupling in assigning vibrational modes in the 1600- to 800-cm^{-1} region or not, there are complications. As mentioned above, five *sets* of methyl vibrations are expected in this region, three deformations and two rocking modes. The deformations are generally assigned between 1500 and 1350 cm^{-1} (see Table V, assignment "set A"). If we assign the two rocks at ca. 907 (referring to each triplet by the most intense band) and ca. 1262 cm^{-1}, several bands are left unassigned. The latter include a triplet at ca. 1197 and a doublet at 1027 cm^{-1}. These are not accounted for by the *two* remaining ν_{CC} assignments.

Because of these difficulties, two different sets of *tert*-butyl assignments (A and B) are given in Table V. The above set of assignments, designated as set A of Table V, is consistent with the traditional *tert*-butyl assignments found in the literature.[24-26]

The second set of *tert*-butyl assignments (Table V, set B) does not require coupling of methyl rock and C–C stretching vibrations. One methyl deformation, δ_{CH_3}, is assigned in the 1300- to 1200-cm^{-1} region to the ca. 1262-cm^{-1} Raman triplet and an infrared doublet, 1250 and 1270 cm^{-1}. This is somewhat lower in energy than is usual for alkanes. The two remaining ν^s_{CC} modes are assigned to bands at 1027 cm^{-1} (uncovered upon isotopic substitution) and 1025 cm^{-1} (^{14}N spectrum). The 1027-cm^{-1} band does not couple to the ν_{NO} and ν_{CO} modes since there is no definite shift upon ^{15}N substitution. The 1027-cm^{-1} band and 1025-cm^{-1} shoulder in the Raman spectrum of the hyponitrite correspond to a pair of bands at 1041 and 1022 cm^{-1} in the Raman spectrum of *tert*-butyl peroxide. The latter were not assigned.[24] We ascribe these to nontotally symmetric CC stretching modes as well. The third infrared-active ν^a_{CC} is tentatively assigned to the 1030-cm^{-1} shoulder. It becomes more prominent as the 990-cm^{-1} band shifts to 980 cm^{-1} with ^{15}N substitution. A similar band is observed in this region in other *tert*-butyl spectra.[24-26]

The latter set B assignments clearly designate four sets of triplets in the Raman spectrum as methyl bending modes. The symmetric and asymmetric C–H stretches form triplets as mentioned above. The spectra can therefore be assigned without resort to ρ_{CH_3}–ν_{CC} coupling arguments. A small isotopic shift at 1198 cm^{-1} (≤ 2 cm^{-1}), however, appears to be real and would suggest some coupling of this $\rho^a_{CH_3}$ to a mode involving nitrogen motion. This could imply skeletal character in accord with assignments of set A.

Weak bands at 1474 and 1425 cm^{-1} may be overtone or combination modes. Solid-state splitting does not explain their appearance since they exist in solution as well.

Assignment of δ_{CC_3}, ρ_{CC_3}, and τ_{CH_3}. These modes (see Table V) are ascribed to bands between 462 and 248 cm^{-1} by direct analogy with the assignments made by Durig et al. for a series of *tert*-butyl derivatives.[27] The band at 108 cm^{-1} may be assigned to an external, lattice mode.

Conclusions

The X-ray data conclusively show that the common form of *tert*-butyl hyponitrite has the trans structure. This information and isotopic substitution allows assignment of characteristic ν_{NN}, ν_{NO}, and ν_{CO} modes, together with related bending modes. The skeletal mode assignments demonstrate mutual exclusion, consistent with the trans structure in both solid-state and solution spectra. The vibrational bands of *tert*-butyl origin have also been assigned. Infrared-Raman u–g splitting varies from 77 cm^{-1} for skeletal modes to <10 cm^{-1} for the more remote *tert*-butyl modes. Similarities between other *tert*-butyl spectra and those reported herein suggest that it may be misleading to interpret spectra in terms of E modes and assumed C_{3v} symmetry.

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Registry No. *trans*-Di-*tert*-butyl hyponitrite, 82554-97-0; *tert*-butyl hyponitrite, 82554-98-1; $Na_2N_2O_2$, 82554-99-2; $NaNO_2$, 68378-96-1.

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Absolute Rate Constants for the Addition of Triethylsilyl Radicals to the Carbonyl Group[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received December 28, 1981*

Abstract: The absolute rate constants for the reactions of $Et_3Si\cdot$ radicals with a large number of carbonyl-containing compounds have been measured in solution by using laser flash photolysis for compounds having rate constants $>10^5$ M^{-1} s^{-1} and kinetic EPR spectroscopy for compounds having rate constants $<10^5$ M^{-1} s^{-1}. The reactivities have a wide range, e.g., the rate constants at ca. 300 K are 2.5×10^9, 3.3×10^8, 1.6×10^6, 2.8×10^5, and 3.5×10^4 M^{-1} s^{-1} for duroquinone, benzil, propionic anhydride, diethyl ketone, and ethyl formate, respectively. Arrhenius parameters were determined for a few representative substrates. Thus for benzil, $E_a = (1.02 \pm 0.09)$ kcal/mol and $\log (A/\text{M}^{-1}\,\text{s}^{-1}) = 9.26 \pm 0.07$. Polar effects are very important in determining the reactivity of carbonyl-containing compounds toward $Et_3Si\cdot$ radicals; e.g., reactivities are greatly enhanced by neighboring perfluoroalkyl and acyloxy groups.

It has been known for some years that silanes add across the carbonyl group of ketones in the presence of free radical initiators[3,4] and that the products formed indicate that the silyl radical adds to the oxygen atom of the carbonyl group.[4] The occurrence of

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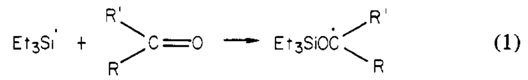
reaction 1 was substantiated in 1969 when Hudson and Jackson[5]



$$\mathrm{Et_3Si}\cdot + \mathrm{R'(R)C{=}O} \longrightarrow \mathrm{Et_3SiO\dot{C}R'(R)} \tag{1}$$

observed the electron paramagnetic resonance (EPR) spectra of the $Et_3SiO\dot{C}Me_2$ and $Et_3SiO\dot{C}(OH)CF_3$ radicals when $Et_3Si\cdot$ was generated in the presence of acetone and of trifluoroacetic acid, respectively. Since that time, more detailed EPR studies by these workers have served to define some of the types of carbonyl-containing compounds to which the triethylsilyl radical will add.[6-10] The ease of addition was reported to decrease in the order: 1,2-diketones > oxalates > ketones > trifluoroacetates > formates > acetates.[7] Several other research groups have also investigated the radicals formed by the addition of trialkylsilyl radicals to carbonyl groups using EPR spectroscopy.[11-19] Of special relevance to the present paper are Neumann and co-workers[11-13] studies of the adduct radicals formed with dialkyl ketones,[11] alkyl aryl ketones,[11] diaryl ketones,[11,12] and benzil;[13] Wan and co-workers[14-17] study of the adducts formed with 2,6-di-*tert*-butylbenzoquinone;[14,15,18] and Krusic et al.'s study of the adducts formed with fluoro ketones.[19] However, in none of these later studies was there any attempt to measure even the relative reactivities of the various carbonyl compounds toward the silyl radical. The complete absence of quantitative rate data for this important class of reactions[20] prompted the present detailed investigation of the rates of addition of triethylsilyl radicals to a wide variety of carbonyl-containing compounds. The experimental techniques employed have been laser flash photolysis and EPR spectroscopy. The enormous variation in reactivity which was encountered is indicated by the fact that at 300 K k_1 ranged from 2.5×10^9 M^{-1} s^{-1} for duroquinone to less than 10^3 M^{-1} s^{-1} for methyl acetate.

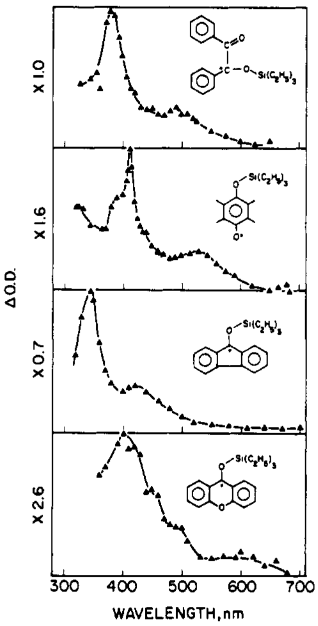


Figure 1. Spectra of the adduct radicals obtained by reaction of triethylsilyl with benzil, duroquinone, fluorenone, and xanthone (all at 27 °C).

Results

Laser Flash Photolysis. General Remarks. In principle this technique allows k_1 to be measured directly by monitoring either the decay of a reagent or the growth of the product of the reaction. However, such a "customized" approach can require a detailed spectroscopic analysis for each reagent or product, which is hardly suitable for a study which was intended to be a comprehensive survey of a large class of reactions. We therefore concentrated our initial efforts on discovering a suitable probe reaction. This approach has proved most successful in earlier kinetic work with other radicals, e.g., *tert*-butoxyl.[22] The probe used in the present study is the addition of $Et_3Si\cdot$ to benzil,[21] one of the reactions examined in the early stages of this work. Other carbonyl compounds that could serve as suitable probes (e.g., duroquinone) were discovered later.

All the experiments described in this section were carried out under oxygen-free conditions by using for excitation the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser.

Generation of Triethylsilyl Radicals. A convenient method for generating trialkylsilyl radicals, which has been widely employed by EPR spectroscopists,[5-7,9,10,14,17-19] involves the photodecomposition of di-*tert*-butyl peroxide in the presence of the silane, viz., eq 2 and 3.

$$\mathrm{Me_3COOCMe_3} \xrightarrow{h\nu} \mathrm{2Me_3CO}\cdot \tag{2}$$

$$\mathrm{Me_3CO}\cdot + \mathrm{Et_3SiH} \rightarrow \mathrm{Me_3COH} + \mathrm{Et_3Si}\cdot \tag{3}$$

The transient absorptions due to *tert*-butoxyl are too weak to be convenient for kinetic studies.[21] The same tends to be true for $Et_3Si\cdot$ which shows weak absorptions below 340 nm.[21,23] The most convenient way to measure k_3 was therefore to use the previously developed diphenylmethanol probe technique,[22] which relies on monitoring the easily detectable signals from diphenylhydroxymethyl radicals. At 300 K in benzene: di-*tert*-butyl peroxide (1:2, v/v) as solvent we obtained $k_3 = (5.7 \pm 0.6) \times 10^6$ M^{-1} s^{-1}.[21,23] At high triethylsilane concentrations the formation of the triethylsilyl radical will therefore be a sufficiently "instantaneous" process that time-resolved studies on their further reactions can be made.

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Table I. Arrhenius Parameters for the Addition of Triethylsilyl Radicals to Certain Carbonyl Compounds

substrate	method[a]	temp range/K	log (A/M^{-1} s^{-1})[b]	E[b]/ kcal mol^{-1}
$[CH_3CH_2C(O)]_2O$	D(378)	256–321	8.03 ± 0.38	2.51 ± 0.51
benzil	D (378)	246–315	9.26 ± 0.07	1.02 ± 0.09
acetophenone	D(378)	243–327	9.40 ± 0.38	3.16 ± 0.49
propionaldehyde	B	249–321	7.81 ± 0.31	0.99 ± 0.41
$[CF_3CF_2C(O)]_2O$	D(378)	226–328	8.91 ± 0.07	0.20 ± 0.09
ethyl formate	E		8.27 ± 0.93	5.12 ± 1.02
ethyl formate	E	161–263	−3.30 ± 0.33	2.70 ± 0.31[c]
ethyl formate	E	230–310	11.57 ± 0.60	2.42 ± 0.71[d]

[a] Methods D and B involve laser flash photolysis:D = direct monitoring of the adduct radical, the monitoring wavelength (in nm) is given in parentheses; B = benzil-probe method, the monitoring wavelength was 378 or 380 nm. Method E involved kinetic EPR spectroscopy. [b] Errors represent 95% confidence limits. [c] Data refer to $k_1/2k_{10}$. [d] Data refer to $2k_{10}$ in units of M^{-1} s^{-1}.

Addition of $Et_3Si\cdot$ Radicals to Benzil. During the initial survey of triethylsilyl radical addition to ketones, benzil was tested. It proved to be well suited for the direct measurement of the absolute rate constants for addition because its own absorptions are relatively weak at the exciting wavelength (ϵ_{337} 120 M^{-1} cm^{-1}), thereby allowing the selective excitation of the di-*tert*-butyl peroxide.[24] Furthermore, the structure of the triethylsilyl–benzil adduct radical has been firmly established as **1** by EPR spectroscopy.[7,8,13]

$$Et_3Si\cdot + PhCOCOPh \rightarrow \underset{\mathbf{1}}{Ph\dot{C}(OSiEt_3)COPh} \quad (4)$$

The generation of $Et_3Si\cdot$ in a 1:1 (v/v) mixture of di-*tert*-butyl peroxide and triethylsilane[25] containing $4 \times 10^{-4} - 5 \times 10^{-3}$ M benzil led to a transient spectrum strongly resembling that of $Ph\dot{C}(OH)COPh$,[26] with maxima at 378 (strong) and 490 nm (weak); see Figure 1.

The rate constant for reaction 4 was obtained from a study of the buildup traces for **1** at different concentrations of benzil. Special care was taken to work under conditions where the experimental lifetime associated with the buildup was considerably longer than the lifetime for $Et_3Si\cdot$ formation via reaction 3. Under these conditions the pseudo-first-order rate constant associated with the buildup, k_{exptl}, is given by

$$k_{exptl} = k_0 + k_4[PhCOCOPh] \quad (5)$$

where k_0 includes all pseudo-first-order modes of decay other than reaction with benzil. Studies in the 246–315 K temperature range yielded the Arrhenius parameters listed in Table I and $k_4 = 3.3 \times 10^8$ M^{-1} s^{-1} at 300 K. Full kinetic data are available as supplementary material.

Addition of $Et_3Si\cdot$ Radicals to Other Carbonyl-Containing Compounds. (1) Using Benzil as the Probe. Many carbonyl compounds readily gave triethylsilyl adduct radicals, reaction 1, but the adducts could not be easily detected by optical means. For these compounds, the rate constants for addition, k_1, were measured by using reaction 4 as the probe. Under competitive conditions where the $Et_3Si\cdot$ radicals can add to RR′C=O or to benzil, the formation of the benzil adduct (which was monitored at 378 or 380 nm) follows pseudo-first-order kinetics which can be described by

$$k_{exptl} = k_0 + k_4[PhCOCOPh] + k_1[RR'C{=}O] \quad (6)$$

where the terms have the same meaning as in eq 5. Values of k_1 at ca. 300 K were determined by this procedure for a wide variety of carbonyl compounds. The results are summarized in Table II, full kinetic details being available as supplementary material. It should be added that k_1 values below ca. 5×10^5 M^{-1} s^{-1} are subject to considerable error and that our laser flash system is unsuited for measuring k_1 values that are smaller than ca. 1×10^5 M^{-1} s^{-1}. The Arrhenius parameters for those few carbonyl compounds which were examined over a range of temperatures are summarized in Table I.

Table II. Absolute Rate Constants for the Addition of Triethylsilyl Radicals to Carbonyl Compounds

substrate	method[a]	T/K	k_1[b]/M^{-1} s^{-1}
duroquinone	D (412)	296	$(2.5 \pm 0.5) \times 10^9$
duroquinone	B	302	$(2.2 \pm 0.1) \times 10^9$
fluorenone	D (355)	301	$(1.5 \pm 0.1) \times 10^9$
$[CF_3CF_2C(O)]_2O$	B	300	$(5.7 \pm 0.7) \times 10^8$
benzaldehyde	B	307	$(4.1 \pm 0.9) \times 10^8$
benzil	D (378)	300	$(3.3 \pm 0.3) \times 10^8$
xanthone	D (410)	304	$(2.4 \pm 0.2) \times 10^8$
p-anisaldehyde	B	297	$(1.7 \pm 0.1) \times 10^8$
benzophenone	*c*	300	$(3.0 \pm 0.6) \times 10^7$
propionaldehyde	B	300	$(1.2 \pm 0.1) \times 10^7$
acetophenone	B	300	$(1.2 \pm 0.1) \times 10^7$
$[CH_3CH_2OC(O)]_2$	B	303	$(5.7 \pm 0.3) \times 10^6$
$CF_3C(O)O(CH_2)_3CH_3$	B	303	$(3.5 \pm 1.3) \times 10^6$
$C_6H_5C(O)OCH_3$	B	306	$(2.8 \pm 0.4) \times 10^6$
$[CH_3CH_2C(O)]_2O$	B	300	$(1.6 \pm 0.6) \times 10^6$
cyclopentanone	B	303	$(7.2 \pm 1.2) \times 10^5$
cyclohexanone	B	303	$(6.6 \pm 1.1) \times 10^5$
cyclobutanone	B	303	$(6.5 \pm 1.8) \times 10^5$
$(C_2H_5)_2CO$	B	301	$(2.8 \pm 0.8) \times 10^5$
ethyl formate	E	300	$(3.5 \pm 2.5) \times 10^4$
$CH_3C(O)OCH_3$	E	243	$<10^2$

[a] Methods D and B involve laser flash photolysis: D = direct monitoring of the adduct radical, the monitoring wavelength (in nm) is given in parentheses; B = benzil probe method, the monitoring wavelength was 378 or 380 nm. Method E involved kinetic EPR spectroscopy. [b] These rate constants correspond to the overall reactivity of the substrate. They have not been statistically corrected for the number of carbonyl groups. [c] See text, using fluorenone as probe.

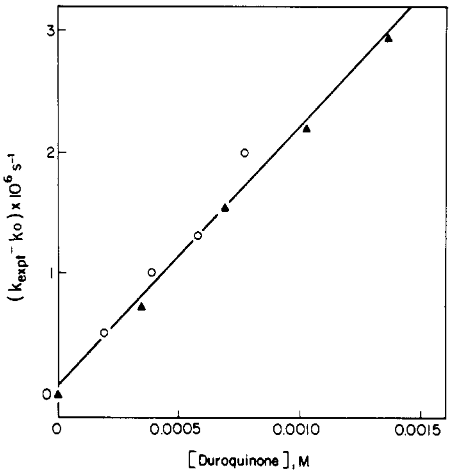

Figure 2. Plot of the experimental pseudo-first-order rate constant (corrected for k_0) for the reaction of triethylsilyl with duroquinone at 27 °C, using direct (○) and probe (▲) techniques.

(2) Using Direct Detection of the Adduct Radical. (i) Duroquinone and Fluorenone. These compounds were found to behave in much the same manner as benzil, giving readily detectable triethylsilyl adduct radicals. The spectra of these two adduct radicals are shown in Figure 1. Duroquinone was used to check the reliability of benzil as a probe. The value of k_1 found at 300 K by the direct method (viz., 2.5×10^9 M^{-1} s^{-1}) was in excellent agreement with the value found by using the benzil probe (viz., 2.2×10^9 M^{-1} s^{-1}). Figure 2 shows a comparison of the results obtained by the two techniques. Values of k_1 for duroquinone and fluorenone are given in Table II together with the wavelengths at which the growth of the adduct radicals were monitored.

(ii) Xanthone. A Case for a Relay Mechanism. Xanthone has a strong absorption maximum at 334 nm (ϵ 9100 M^{-1} cm^{-1}) which

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[25] High concentrations of both reagents are necessary to ensure that most of the light is absorbed by the peroxide and the $Et_3Si\cdot$ formation is "instantaneous".

[26] In the case of $C_6H_5\dot{C}(OH)COC_6H_5$ the weak band is located at ~500 nm and the strong one at $\lambda < 370$ nm.[24]

is almost coincident with the wavelength used for excitation (337 nm). At concentrations which would allow the growth of the triethylsilyl adduct radical to be easily monitored we expected a predominant excitation of xanthone, leading to interference by its triplet state and a decrease in free radical production, and thus signal. To our surprise, on following normal procedures with xanthone concentrations of 5.8×10^{-4} to 3.3×10^{-3} M in di-*tert*-butyl peroxide: Et_3SiH (1:1, v/v) as solvent, excellent kinetic traces were obtained from which k_1 was readily calculated (see Table II). There can be no doubt that the laser light was largely absorbed by the xanthone rather than by the peroxide.[27] We therefore propose that xanthone triplets (Xan*) sensitize the decomposition of the peroxide (eq 7).[28] From a comparison with

$$\text{Xan}^* + Me_3COOCMe_3 \rightarrow \text{Xan} + 2Me_3CO\cdot \qquad (7)$$

other sensitizers we estimate that k_8 is ca. 8×10^6 M^{-1} s^{-1}.[28,29] This reaction makes the absorption of light by the xanthone formally equivalent to absorption by the peroxide, thus making the kinetic analysis identical to that for benzil. The spectrum of the xanthone adduct radical is shown in Figure 1.

(iii) Benzophenone. The extinction coefficient of benzophenone at 337 nm is sufficiently high, that some of the light in this system is always absorbed by benzophenone. This leads to the triplet state that can decay via hydrogen abstraction from Et_3SiH or through sensitization of the decomposition of di-*tert*-butyl peroxide. Since all the rate constants involved are known,[23,28] it is straightforward to predict the decay pathways of benzophenone triplets in, e.g., a 1:1 mixture of Et_3SiH and di-*tert*-butyl peroxide; i.e., the triplet lifetime will be ca. 20 ns and 80% of the triplets will decay via hydrogen abstraction, to generate a ketyl and a triethylsilyl radical.

Our initial attempts to measure the kinetics of this system, both by direct detection and with use of benzyl as a probe, were systematically unsuccessful. A steady-state photolysis study, using UV spectroscopy to monitor the changes taking place, showed that irradiation of benzophenone–Et_3SiH systems with or without peroxide leads not only to the efficient destruction of benzophenone but also to the formation of reaction products with strong absorptions at $\lambda < 350$ nm. These products may account for only a small percentage of reaction, but their absorption in the excitation region makes them play a critical role. While their structure was not established, they probably result from radical–molecule or radical–radical reactions similar to those leading to LATs (for light absorbing transients), which are well documented in the photochemistry of benzophenone.[30-38]

In view of the formation of UV-screening products and the efficient consumption of benzophenone, it is hardly surprising that these measurements were particularly difficult. In an attempt to overcome these problems, we carried out a series of experiments in a flow system, so that product accumulation could be avoided, and with the highly reactive fluorenone as the probe. These experiments were carried out in a 3:7 (v/v) Et_3SiH/di-*tert*-butyl peroxide solvent. They led to the benzophenone k_1 value included in Table II.

Exploratory experiments using 4,4′-dimethylbenzophenone suggested that its behavior is very similar to that of benzophenone.

Kinetic EPR Spectroscopy. General Remarks. The laser flash photolytic procedure cannot be used with carbonyl compounds for which k_1 is less than ca. 1×10^5 M^{-1} s^{-1}. This is because even with relatively high concentrations of such unreactive substrates decay of triethylsilyl radicals by their diffusion-controlled bimolecular self-reactions become competitive. Fortunately, a simple kinetic EPR spectroscopic technique allows rate constants for radical–molecule reactions that are in the range ca. 10^3–10^5 M^{-1} s^{-1} to be measured, provided both the initial radical (viz., $Et_3Si\cdot$) and the product radical (viz., $Et_3SiO\dot{C}RR'$) can be observed simultaneously.[39,40] In essence, samples containing Et_3SiH, di-*tert*-butyl peroxide, and a known concentration of the carbonyl compound in an inert solvent, or in the absence of solvent, are photolyzed directly in the cavity of an EPR spectrometer. Triethylsilyl radicals are formed by reactions 2 and 3, and the adduct radical is formed by reaction 1. These two radicals are destroyed by the following three reactions.

$$Et_3Si\cdot + Et_3Si\cdot \rightarrow \text{nonradical products} \qquad (8)$$

$$Et_3Si\cdot + Et_3SiO\dot{C}RR' \rightarrow \text{nonradical products} \qquad (9)$$

$$Et_3SiO\dot{C}RR' + Et_3SiO\dot{C}RR' \rightarrow \text{nonradical products} \qquad (10)$$

Provided the adduct radical is sterically unprotected at its radical center, it can be safely assumed[41] that all of these radical–radical reactions are proceeding at the diffusion-controlled rate. In such a case, under conditions of steady photolysis, where the radical concentrations do not change with time, we can write[40]

$$\frac{k_1[RR'CO]}{2k_{10}} = [Et_3SiO\dot{C}RR']\left(1 + \frac{[Et_3SiO\dot{C}RR']}{[Et_3Si\cdot]}\right) \qquad (11)$$

Measurements of the absolute concentrations of the two radicals at a known concentration of RR′CO will therefore yield $k_1/2k_{10}$. The value of $2k_{10}$ can be readily determined in a separate experiment[41] and hence k_1 is obtained.

Under typical experimental conditions free radicals which undergo bimolecular self-reactions at the diffusion-controlled limit can be photogenerated at concentrations of ca. 10^{-7} M.[41] With the assumption that both $Et_3Si\cdot$ and $Et_3SiO\dot{C}RR'$ radicals are present together at this concentration and that $2k_{10}$ has a (typical) value of 5×10^9 M^{-1} s^{-1}, then $k_1[RR'CO]$ will be 10^3 s^{-1}. By the same token, if only triethylsilyl radicals can be observed, then $k_1[RR'CO]$ must be less than 10^3 s^{-1}. If this is the situation at high concentrations (≥ 1 M) of RR′CO, it is safe to assume than $k_1 \leq 10^2$ M^{-1} s^{-1}.

Addition of $Et_3Si\cdot$ Radicals to Ethyl Formate. Cooper, Hudson, and Jackson[7] have reported that when $Et_3Si\cdot$ radicals are generated in the presence of methyl or ethyl formate, both the $Et_3Si\cdot$ and the adduct radicals can be observed at temperatures from 173 to 273 K and that the concentration of the adduct radical increases relative to that of $Et_3Si\cdot$ with increasing temperature. We have confirmed and quantified this result for ethyl formate. In Table I are listed the Arrhenius parameters measured for the rate constant ratio $k_1/2k_{10}$ and for $2k_{10}$, the latter being measured by the usual kinetic EPR method,[41] plus the derived parameters for the addition of $Et_3Si\cdot$ radicals to the formate. The experimental data are given as supplementary material.

Cooper et al.[7] also reported that no adduct was formed from $Et_3Si\cdot$ radicals and methyl acetate at temperatures from 173 to 283 K. We have confirmed their result. Since we were unable to observe any radical other than $Et_3Si\cdot$ at temperatures as high as 243 K in the presence of 4.2 M methyl acetate, we conclude that for this compound $k_1 < 1.0 \times 10^2$ M^{-1} s^{-1}. (At temperatures above 243 K a variety of other radicals were formed; none of these

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(27) Note that with benzil, duroquinone, etc., it is the peroxide which absorbs most of the light.

(28) Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640–645.

(29) In studies of free radicals it has sometimes been found useful to sensitize the decomposition of di-*tert*-butyl peroxide: see, Griller, D.; Ingold, K. U.; Scaiano, J. C. *J. Magn. Reson.* **1980**, *38*, 169–171.

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(39) For some reactions for which this technique has been employed, see: Hellebrand, J.; Wünsche, P. *Faserforsch. Textiltech.* **1976**, *27*, 621–623. Shiraishi, H.; Ranby, B. *Chem. Scr.* **1977**, *12*, 118–124. Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1979**, 373–374.

(40) For a review of other applications of the same technique, see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

(41) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193–200.

appeared to be the adduct radical.)

Discussion

The results of this work, which are summarized in Tables I and II, greatly extend and generally confirm the conclusions of Cooper, Hudson, and Jackson[7] regarding the relative rates of reaction 1 for various types of carbonyl groups. The only significant difference to their order of reactivity is that trifluoroacetate is actually more reactive than dialkyl ketones rather than being less reactive. Our quantitative kinetic data reveal that there is an enormous spread in the reactivities of different types of carbonyl groups. Cooper et al.[7] rationalized their results in terms of bond energy differences, stabilization of radicals formed, and polar effects. Steric factors were considered to be relatively unimportant, but our results do suggest that they play a role (vide infra). Since we do not wish merely to repeat either their arguments or those made by us with respect to the polar effect in the following paper which describes halogen atom abstractions by $Et_3Si\cdot$ radicals,[42] only the more salient features of our results will be discussed.

Duroquinone and, presumably, other 1,4-benzoquinones react very rapidly with triethylsilyl radicals. Since the resultant adduct radicals are often persistent, the utility of this class of compounds as spin traps for silicon-centered and other group 4 metal-centered radicals[14,17,18] can be readily understood.

The high reactivity of carbonyls bearing an adjacent phenyl group can obviously be attributed to stabilization of the adduct radical by electron delocalization into the substituent. The same is doubtless true of 1,2-diketones. The high reactivity of carbonyls bearing an adjacent perfluoroalkyl group can be attributed to polar effects. That is, if the transition state is represented by the canonical structures

$$Et_3Si\cdot O{=}CRR' \leftrightarrow Et_3Si{-}O{-}\dot{C}RR' \leftrightarrow Et_3Si^+O^-{-}\dot{C}RR'$$

it becomes clear why an electron-withdrawing perfluoroalkyl group will tend to stabilize the transition state since it will stabilize the negative charge on the carbonyl group. A similar argument explains why anhydrides are so much more reactive than esters since an acyloxy group, RC(O)O, is clearly much more strongly electron withdrawing than is an alkoxy group, RO. In this connection, Cooper et al.[7] pointed out that although the relatively low reactivity of esters was probably due mainly to ground-state stabilization of their C=O double bond by the (p-type) lone pair on the alkoxy group's oxygen, unfavorable polar effects might also play a role since esters accept an electron less readily than ketones.

Cyclic ketones are slightly more reactive than their acyclic counterparts. We attribute this result to the carbonyl groups being sterically less well protected in the cyclic compounds. Similarly, we suggest that the higher reactivity of aldehydes compared with ketones and of formates compared with acetates is due in some part to steric factors.

Finally, our results allow us to expand Cooper et al.'s reactivity order for carbonyl groups to 1,4-benzoquinone $\gtrsim$ cyclic diaryl ketones, benzaldehyde, benzil, perfluoroacid anhydride > benzophenone ≫ alkyl aryl ketone, alkyl aldehyde > oxalate > benzoate, trifluoroacetate, anhydride > cyclic dialkyl ketone > acyclic dialkyl ketone > formate > acetate. Over this series of compounds the rate constants for $Et_3Si\cdot$ radical addition vary by more than 6 orders of magnitude.

Registry No. 1, 51226-72-3; $Et_3Si\cdot$, 24669-77-0; $[CF_3CF_2C(O)]_2O$, 356-42-3; $[CH_3CH_2OC(O)]_2$, 95-92-1; $CF_3C(O)O(CH_2)_3CH_3$, 367-64-6; $C_6H_5C(O)OCH_3$, 93-58-3; $[CH_3CH_2C(O)]_2O$, 123-62-6; $(C_2H_5)_2CO$, 96-22-0; $HC(O)OC_2H_5$, 109-94-4; $CH_3C(O)OCH_3$, 79-20-9; benzil, 134-81-6; propionaldehyde, 123-38-6; duroquinone, 527-17-3; fluorenone, 486-25-9; benzophenone, 119-61-9; benzaldehyde, 100-52-7; xanthone, 90-47-1; *p*-anisaldehyde, 123-11-5; acetophenone, 98-86-2; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cyclobutanone, 1191-95-3; 4-(triethylsilyloxy)-2,3,5,6-tetramethylphenoxy, 82414-91-3; 9-(triethylsilyloxy)fluoren-9-yl, 82414-92-4; 9-(triethylsilyloxy)xanthen-9-yl, 82414-93-5.

Supplementary Material Available: Tables giving detailed kinetic data (33 pages). Ordering information is given on any current masthead page.

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[42] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C., following paper in this issue.

Absolute Rate Constants for the Reaction of Triethylsilyl Radicals with Organic Halides[1]

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Abstract: The absolute rate constants for the reactions of $Et_3Si\cdot$ radicals with a number of organic halides have been measured in solution by using laser flash photolysis techniques. The reactivities cover a wide range; e.g., the rate constants at ca. 300 K are 4.3×10^9, 1.1×10^8, 2.5×10^6, and $<10^5$ M^{-1} s^{-1} for CH_3CH_2I, C_6H_5Br, $(CH_3)_3CCl$, and $C_6H_5CH_2F$, respectively. Arrhenius parameters were determined for a few representative substrates. Thus, for CCl_4, $E_a = (0.78 \pm 0.24)$ kcal/mol and $\log (A/M^{-1}\ s^{-1}) = 10.2 \pm 0.2$, data which can be combined with relative rates from the literature to yield absolute rate constants for some additional substrates. Comparison of the Arrhenius parameters for halogen abstraction from several substrates suggests the involvement of charge-transfer interactions in some of these reactions. Such rate-enhancing interactions can have a greater influence on the preexponential factor than on the activation energy. An explanation for this phenomenon is advanced. Combination of our rate constants with data from literature also allows evaluation of the rates of inversion at the silicon center in triorganosilyl radicals as being in the range $(3\text{-}12) \times 10^9$ s^{-1} at temperatures from 0 to 80 °C which implies that a considerable activation barrier is involved in such processes.

Many heteroatom-centered free-radicals are capable of removing a halogen atom from suitable organic halides. In some cases, this process is presumed to be a simple halogen atom abstraction, i.e., eq 1. In other cases an electron transfer is probably

$$R'_nM\cdot + RX \rightarrow R'_nMX + R\cdot \qquad (1)$$

involved, i.e., eq 2. Heteroatoms for which such processes have

$$R'_nM\cdot + RX \rightarrow (R'_nM^+RX^-\cdot) \rightarrow R'_nMX + R\cdot \qquad (2)$$

been identified include, for example, boron,[3] silicon,[4-15] germa-

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