J. Am. Chem. Soc. **1984**, *106*, 343–348

Kinetic Analyses. Phosphate buffer, 0.050 M, pH 12.5, was mixed with an equal volume of *tert*-butyl alcohol. Esters of approximately 1×10^{-2} M were dissolved in acetonitrile. Reactions are initiated by injecting 100 μL of the ester solutions into a cuvette containing 3.0 mL of the butanol–phosphate buffer which had previously been brought to the desired temperature in a Perkin-Elmer Model 571 spectrophotometer. After mixing the solution of ester in butanol–phosphate buffer, the optical density at 287 nm due to the formation of 3,4,5-trimethoxyphenol was recorded on a digital printer during the course of the first 3% of the reaction. Best fit linear regressions of these straight line regions ($r \geq 0.990$) afforded the initial rates in OD/s which were then converted to mol/L·s by dividing by the extinction coefficient of 3,4,5-trimethoxyphenol in the butanol–buffer mixture, the ester concentration in the cuvette, and the calculated hydroxide ion concentration. Analyses were performed at least three times on each ester at each temperature, 20, 30, and 40 °C.

Preparation of Ethylene Ketals of 1-Adamantyl Methyl Ketone and *tert*-Butyl Methyl Ketone. Ethylene glycol and a few milligrams of *p*-toluenesulfonic acid were reacted in benzene with 1-adamantyl methyl ketone and pinacolone, respectively, by azeotropic distillation of water. The crude ethylene ketals obtained after the usual workup were purified by either fractional distillation or preparative vapor phase chromatography. Physical and spectroscopic characteristics were identical with the literature[26] values in the case of the ketal derived from pinacolone. The ketal derived from 1-adamantyl methyl ketone, mp 52–53 °C, evinced spectroscopic and elemental analyses consistent with its formulation.

Heats of Hydrolysis of Ethylene Ketals. The heats of hydrolyses in a 92% aqueous dioxane solution 0.001 N in HCl were measured with an LKB 8721-4 closed bomb reaction calorimeter in combination with an LKB 8700 Precision calorimetry system. The calibration of the calorimeter was accomplished by using THAM. For this part the calorimeter vessel was filled with 60 mL of 0.102 M HCl. The reaction was carried out in a thermostat which was controlled at 25.00 ± 0.01 °C. Resistance–time measurements were obtained to give a sufficiently long post-reaction period, about 10 min after thermal equilibrium had been reached.

Acknowledgment. This research was supported by the American Chemical Society (PRF No. 11305-B4). The microcalorimeter used in determining heats of ketal hydrolysis was obtained by Drs. Tomkins and A. Greenberg as a Research Corp. grant. We thank the following students for their help: R. Kapichak, M. Lang, T.-W. May, T. Roberto, P. Simon, and W. Smith. We gratefully acknowledge the following persons for their generous donation of samples: Drs. P. Chenier (2-bicyclo[2.2.1]heptene-1-carboxylic acid), C. Grob (bicyclo[2.2.2]octane-1-carboxylic acid), D. Jakas (bicyclo[3.2.1]octane-1-carboxylic acid), J. Kauer (bicyclo-[2.2.1]heptane-1-carboxylic acid), T. Kawamura (bicyclo-[2.1.1]hexane-1-carboxylic acid), D. Martella (2-methyl-2-adamantanol), and C. Rüchardt (bicyclo[3.2.2]nonane-1-carboxylic acid).

Registry No. 2, 87901-92-6; **3**, 87901-93-7; **4**, 87901-94-8; **5**, 87901-96-0; **6**, 87921-91-3; **7**, 87901-97-1; **8**, 87901-98-2; 9, 87901-99-3; **10**, 87902-00-9; **11**, 87902-01-0; **12**, 87902-02-1; **13**, 87901-95-9.

Absolute Rate Constants for the Reactions of Tri-*n*-butylgermyl and Tri-*n*-butylstannyl Radicals with Carbonyl Compounds, Other Unsaturated Molecules, and Organic Halides[1]

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Abstract: The absolute rate constants for the reactions of n-Bu$_3$Ge· and n-Bu$_3$Sn· radicals with a wide variety of organic compounds have been measured in solution at ca. 300 K by using laser flash photolysis techniques. For most of the substrates examined the n-Bu$_3$Ge· and n-Bu$_3$Sn· radicals were found to have essentially equal reactivity, e.g., the measured rate constants were 7.4×10^8 and 1.4×10^9 M^{-1} s^{-1}, respectively, for duroquinone; 9.6×10^7 and 1.3×10^8 M^{-1} s^{-1}, respectively, for benzil; 8.6×10^7 and 9.9×10^7 M^{-1} s^{-1}, respectively, for styrene; 4.6×10^7 and 6.8×10^7 M^{-1} s^{-1}, respectively, for 1,4-pentadiene; and 8.6×10^7 and 1.7×10^8 M^{-1} s^{-1}, respectively, for *tert*-butyl bromide. In all their reactions, these two radicals are less reactive than triethylsilyl radicals. From literature data we are able to estimate that the inversion of triorganogermyl radicals is somewhat slower than that for triorganosilyl radicals.

Absolute rate constants for a wide variety of reactions involving carbon-centered radicals are available,[3] but the same cannot be said for radicals centered on the other atoms from group 4.

For silicon-centered radicals the most extensive (and almost the only) absolute rate data come from our own recent work. We have measured rate constants for the formation of silyl radicals by H-atom abstraction from the parent silanes,[4-6] for the addition of triethylsilyl radicals to carbonyl compounds[4,7] and other classes of unsaturated compounds,[8] and for halogen atom abstractions by triethylsilyl.[4,9]

Considerably less information is available regarding the absolute reactivity of tin-centered radicals. Rotating sector studies, which were reported from this laboratory in 1968,[10,11] yielded rate constants for H-atom abstraction from tri-*n*-butyltin hydride (and

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a few other tin hydrides) by carbon-centered radicals and rate constants for halogen-atom abstraction by the n-$Bu_3Sn\cdot$ radical. Subsequent rotating sector studies yielded rate constants for the reaction of the n-$Bu_3Sn\cdot$ radical with some disulfides[12] and peroxides.[13] More recently, the reaction of carbon-centered radicals with n-Bu_3SnH has been reexamined by using laser techniques,[14] and the results of the 1968 report[11] have been largely confirmed and considerably expanded. Other recent reports have provided absolute rate data on the reaction of the Sn–H bond with alkoxyl radicals,[6,15] ketone triplets,[15] some 1,4-biradicals,[16] and trialkylstannyl radicals.[17,18]

For germanium-centered radicals very little is known about the absolute rates of reactions leading to their formation, or reactions in which they attack organic substrates. Rate constants for H-atom abstraction by *tert*-butoxyl from n-Bu_3GeH and Ph_3GeH have been reported,[6] as have the rate constants for H-atom abstraction from n-Bu_3GeH by methyl and trichloromethyl radicals,[19] and by primary alkyl radicals.[20] There are no absolute rate constants for reactions of germanium-centered radicals with organic molecules. However, we have measured the rate constant for the reaction of n-$Bu_3Ge\cdot$ radicals with oxygen[21] and that for the bimolecular self-reaction of $Me_3Ge\cdot$ radicals.[22] This lack of kinetic data should not, however, be taken to mean that the reactivity pattern for $R_3Ge\cdot$ radicals has not been established. In fact, a considerable volume of information has been gathered since Fischer et al.'s 1954 reference to an addition reaction of a germyl radical.[23] A recent review by Sakurai[24] summarizes our current knowledge of these radicals, most of which has come from product studies and EPR spectroscopy. For example, the ease of addition of $R_3M\cdot$ radicals to carbonyl groups follows the order[24,25]

$$R_3Si\cdot > R_3Ge\cdot \sim R_3Sn\cdot > R_3Pb$$

while the order of reactivities with different carbonyl compounds for $R_3Ge\cdot$ is not unlike the one observed for $R_3Si\cdot$, with diketones showing extremely high reactivity and carboxylic esters being almost unreactive.[7]

In the present work we have employed laser flash photolysis techniques to measure the absolute rates of reaction of n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$ radicals with some carbonyl compounds, some other unsaturated molecules, and some organic halogen atom donors. These studies turned out to be rather difficult, and out of necessity they are somewhat more limited than our earlier reports[4,7-9] on the reactions of $Et_3Si\cdot$ radicals. Nevertheless, they do provide a broad and useful picture of the absolute reactivities of germanium- and tin-centered radicals which should provide a strong base for further, more detailed investigations of such radicals.

Experimental Section

Materials. Tri-n-Butylgermane was prepared by reduction of n-Bu_3GeCl by lithium aluminum hydride.[26] The chloride and all other compounds were commercially available. Before use they were generally purified by standard methods or were already available in purified form in our laboratory.

Laser Flash Photolysis. General Techniques. The samples (usually 1 mL) were contained in 3 × 7 mm^2 cells made of rectangular Suprasil tubing and were deoxygenated by bubbling with oxygen-free nitrogen. A Molectron UV-24 nitrogen laser delivering pulses at 337.1 nm (~8 ns, up to 10 mJ/pulse) was used for excitation. The system, which uses a PDP 11/23 computer for experiment control, data handling, and storage, has been described in detail elsewhere.[27]

Considerable problems were encountered with a number of organohalides because the reactants were rapidly consumed by the well-known radical chain process.[28] To avoid substrate depletion, fresh samples were generally used for each concentration of substrate for which kinetic measurements were made, and the number of laser pulses was reduced to a minimum. For the n-$Bu_3Ge\cdot$/halide reactions for which this problem was acute, e.g., with CH_3I and with n-C_3H_7I, only a lower limit for the rate constant for halogen abstraction could be obtained. However, for the two n-$Bu_3Sn\cdot$/halide reactions that were examined this problem was overcome by the use of a flow system.[29] This was possible because the tin hydride precursor is commercially available and, being substantially more reactive toward H abstraction than its germanium analogue, can be used at lower concentrations. Furthermore, relatively few absolute rate constants were required for the n-$Bu_3Sn\cdot$/halide reactions (vide infra). Typical flow rates were ca. 0.1 mL/pulse.

Kinetic Procedures. Both n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$ radicals show intense UV absorptions at $\lambda < 320$ nm.[6] However, the nature of the experiments is such (vide infra) that the samples were usually not sufficiently transparent in this region to allow the analyzing beam to pass through them, which is an essential requirement in this type of experiment. Fortunately, the absorption spectrum of n-$Bu_3Ge\cdot$ shows a shoulder band in the 350-nm region,[6] and that of n-$Bu_3Sn\cdot$ shows a second band in the 400-nm region.[6,15] These absorptions are weak, particularly in the case of n-$Bu_3Ge\cdot$, but are still adequate for kinetic analysis using signal averaging techniques provided the substrate and/or products of reaction do not have interfering absorptions in these spectral regions. This direct, time-resolved monitoring of changes in the concentrations of the n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$ radicals, which is referred to hereafter as method A, was found to be suitable for most substrates. For n-$Bu_3Ge\cdot$ the monitoring wavelength was 346 nm, since this was found to be the optimum compromise leading to sufficient signal intensity while allowing some separation from the excitation at 337 nm. For n-$Bu_3Sn\cdot$ the monitoring wavelength was 400 nm. The need for signal averaging made the experiments rather difficult in those systems where photoexcitation initiated a chain reaction.

In those reactions in which one of the primary products showed moderately intense absorptions at $\lambda > 345$ nm, it was generally preferable to use the signals derived from product buildup to monitor the kinetics of the reactions.[7] This procedure is referred to hereafter as method B.

The probe technique, method C, which we have used to study silyl,[4,7-9] alkoxyl,[5,6,31,32] and phenyl[30] radicals, involves the use of two substrates, at least one of which yields signals suitable for kinetic analysis. Although one substrate may carry the signal, the absolute rate for the second substrate can be determined.[4-9,30-32] This method was occasionally employed in the present work when unusual difficulties were encountered when methods A and B were used. However, in no case did method C yield data that were better than the data obtained by one of the other two methods.

It should be noted that rate constants measured by methods A, B, and C are those which correspond to molecular reactivity, i.e., they incorporate all modes and sites of attack on a given substrate regardless of the reaction path that is actually monitored. Furthermore, all three methods require that the formation of the n-$Bu_3Ge\cdot$ or n-$Bu_3Sn\cdot$ radicals is sufficiently rapid that, on the time scale of our experiments, formation can be regarded as an "instantaneous" process. That is, the formation of

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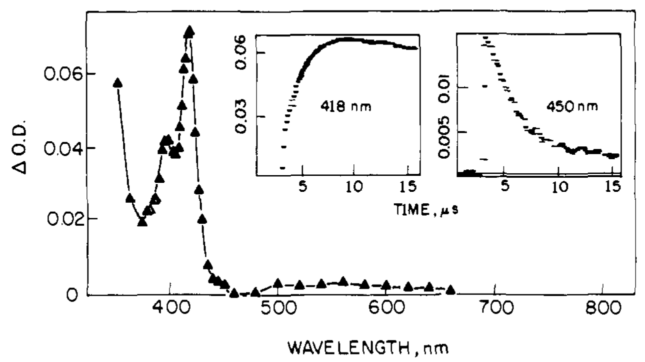


Figure 1. Spectrum of the adduct radical formed by the addition of n-$Bu_3Sn\cdot$ to duroquinone, monitored approximately 7 μs following excitation. The inserts show the decay of n-$Bu_3Sn\cdot$ at 450 nm and the formation of the adduct at 418 nm. The sample contained 0.0035 M duroquinone in a 1:9 (v/v) mixture of n-Bu_3SnH and peroxide.

n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$ must be much faster than their decay. Experiments were carried out in di-*tert*-butyl peroxide containing 15% (v/v) n-Bu_3GeH or 10% (v/v) n-Bu_3SnH as solvent. The metal-centered radicals are formed by the reaction sequence:

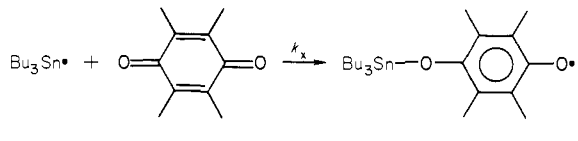
$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO\cdot$$

$$Me_3CO\cdot + n\text{-}Bu_3MH \xrightarrow{k_a} Me_3COH + n\text{-}Bu_3M\cdot$$

Values of k_a have been measured at 300 K: for n-Bu_3GeH $k_a \approx 9 \times 10^7$ M^{-1} s^{-1};[6] and for n-Bu_3SnH $k_a \approx 2 \times 10^8$ M^{-1} s^{-1}.[15] Thus, under our experimental conditions the lifetime for formation of n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$ will be less than 20 ns, which is sufficiently short to satisfy the criteria mentioned above. The high concentration of peroxide assures an adequate absorption at the laser wavelength (337.1 nm).

Results

Addition to Carbonyl Compounds. The reactions of n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$ with duroquinone, fluorenone, and benzil, all of which involve addition to the carbonyl oxygen,[25,33-39] were monitored by method B. As an example, duroquinone reacts with the n-$Bu_3Sn\cdot$ radical to yield an adduct with the absorption spectrum shown in Figure 1.



As would be expected, the spectrum in Figure 1 is similar to that of the duroquinone/triethylsilyl adduct.[7] The inserts in this figure show a representative adduct buildup trace obtained at 418 nm and a representative n-$Bu_3Sn\cdot$ decay trace obtained at 450 nm.[40] These traces can be fitted with a single exponential which yields k_{exptl}, the experimental first-order rate constant for signal buildup, or decay. The experimental rate constant is related to the rate constant for the radical/substrate reaction, k_x, according to the equation

$$k_{\text{exptl}} = k_0 + k_x[\text{substrate}]$$

Table I. Absolute Rate Constants for the Addition of n-$Bu_3Ge\cdot$, n-$Bu_3Sn\cdot$, $Et_3Si\cdot$, and n-$Bu_3Si\cdot$ Radicals to Some Carbonyl Compounds

	n-$Bu_3Ge\cdot$[a]			n-$Bu_3Sn\cdot$[b]			$Et_3Si\cdot$[c]			n-$Bu_3Si\cdot$[d]		
substrate	method[e]	T, K	k,[f] M^{-1} s^{-1}	method[e]	T, K	k,[f] M^{-1} s^{-1}	method[e]	T, K	k,[f] M^{-1} s^{-1}	method[e]	T, K	k,[f] M^{-1} s^{-1}
duroquinone	B	297	$(7.4 \pm 0.3) \times 10^8$	B	298	$(1.4 \pm 0.1) \times 10^9$	B	296	$(2.5 \pm 0.5) \times 10^9$	B	299	$(1.0 \pm 0.1) \times 10^9$
fluorenone	B	298	$(4.7 \pm 0.3) \times 10^8$	B	299	$(3.8 \pm 0.5) \times 10^8$	B	301	$(1.5 \pm 0.1) \times 10^9$	B	298	$(1.1 \pm 0.1) \times 10^9$
$C_6H_5COCOC_6H_5$	B	298	$(9.6 \pm 0.9) \times 10^7$	B	298	$(1.3 \pm 0.1) \times 10^8$	B	300	$(3.3 \pm 0.3) \times 10^8$	B	299	$(2.4 \pm 0.1) \times 10^8$
$[CF_3CF_2C(O)]_2O$	A	297	$(1.3 \pm 0.1) \times 10^8$			nm[g,h]	C	300	$(5.7 \pm 0.7) \times 10^8$			nm[g]
CH_3CH_2CHO	A, C	299	$<1 \times 10^5$			nm[g]	C	300	$(1.2 \pm 0.1) \times 10^7$			nm[g]
cyclohexanone	A	301	$<3 \times 10^4$	A	293	$<5 \times 10^4$	C	303	$(6.6 \pm 1.1) \times 10^5$			nm[g]

[a] Di-*tert*-butyl peroxide + 15% (v/v) n-Bu_3GeH as solvent. [b] Di-*tert*-butyl peroxide + 10% (v/v) n-Bu_3SnH as solvent. [c] Data are from ref 7. Di-*tert*-butyl peroxide/Et_3SiH 1:1 (v/v) as solvent. [d] Di-*tert*-butyl peroxide/n-Bu_3SiH 1:1 (v/v) as solvent. [e] Method A, monitoring of metal-centered radical; B, monitoring of adduct radical; C, probe technique. [f] Errors correspond to two standard deviations. [g] Not measured. [h] The tin hydride and anhydride react spontaneously, see text.

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(40) Monitored at this wavelength rather than at 400 nm to avoid interference by the adduct's absorption.

Table II. Absolute Rate Constants for the Addition of *n*-$Bu_3Ge\cdot$, *n*-$Bu_3Sn\cdot$, and $Et_3Si\cdot$ Radicals to Some Unsaturated Compounds

	n-$Bu_3Ge\cdot$[a]			*n*-$Bu_3Sn\cdot$[b]			$Et_3Si\cdot$[c]		
substrate	method[d]	*T*, K	*k*,[e] $M^{-1}\ s^{-1}$	method[d]	*T*, K	*k*,[e] $M^{-1}\ s^{-1}$	method[e]	*T*, K	*k*,[e] $M^{-1}\ s^{-1}$
$H_2C{=}CHC{\equiv}N$	A	300	$(1.8 \pm 0.3) \times 10^8$	A	299	$(8.8 \pm 0.6) \times 10^7$	C	302	$(1.1 \pm 0.2) \times 10^9$
$H_2C{=}C(CH_3)C(O)OCH_3$	A	300	$(1.2 \pm 0.2) \times 10^8$	A	298	$(1.2 \pm 0.1) \times 10^8$	C	300	$(4.6 \pm 0.8) \times 10^8$
$H_2C{=}CCl_2$	A	301	$(1.0 \pm 0.1) \times 10^8$			nm[f]	C	300	$(2.7 \pm 0.3) \times 10^8$
$H_2C{=}CHC_6H_5$	A	298	$(8.6 \pm 2.6) \times 10^7$	A	297	$(9.9 \pm 0.6) \times 10^7$	C	300	$(2.2 \pm 0.2) \times 10^8$
$H_2C{=}CHCH{=}CHCH_3$ (*cis*)	A	298	$(4.0 \pm 0.4) \times 10^7$	A	298	$(6.8 \pm 0.5) \times 10^7$			nm[f]
$H_2C{=}CHCH{=}CHCH_3$ (*trans*)	A	297	$(4.6 \pm 0.3) \times 10^7$	A	298	$(6.8 \pm 0.3) \times 10^7$	C	299	$(1.4 \pm 0.1) \times 10^8$ [g]
1,3-cyclooctadiene	A	299	$(6.4 \pm 0.3) \times 10^5$	A	297	$<7 \times 10^4$	C	299	$(3.8 \pm 0.4) \times 10^6$ [g]
β-pinene	A	301	$<2 \times 10^5$	A		$<2 \times 10^5$	C	299	$(7.1 \pm 0.4) \times 10^6$ [g]
C_6H_6			nm[f]	A	299	$<2 \times 10^4$	C	296	$(4.6 \pm 1.0) \times 10^5$
$C_6H_5CH_3$	A	300	$<4 \times 10^4$			nm[f]	C	297	$(1.2 \pm 0.2) \times 10^5$

[a] Same as footnote *a*, Table 1. [b] Same as footnote *b*, Table 1. [c] Data are from ref 8 unless otherwise noted. Di-*tert*-butyl peroxide/Et_3SiH 1:1 (v/v) as solvent. [d] Same as footnote *e*, Table 1. [e] Same as footnote *f*, Table I. [f] Not measured. [g] This work.

Table III. Absolute Rate Constants for the Abstraction of Halogen from Some Organic Halides by *n*-$Bu_3Ge\cdot$, *n*-$Bu_3Sn\cdot$, and $Et_3Si\cdot$ Radicals

	n-$Bu_3Ge\cdot$[a]			*n*-$Bu_3Sn\cdot$[b]			$Et_3Si\cdot$[c]			*n*-$Bu_3Sn\cdot$[d]	
substrate	method[e]	*T*, K	*k*,[f] $M^{-1}\ s^{-1}$	method[e]	*T*, K	*k*,[f] $M^{-1}\ s^{-1}$	method[e]	*T*, K	*k*,[f] $M^{-1}\ s^{-1}$	*T*, K	*k*, $M^{-1}\ s^{-1}$
CH_3I	A	301	$>1 \times 10^8$ [g]			nm[h]	C	302	$(8.1 \pm 0.4) \times 10^9$	298	4.3×10^9
$CH_3CH_2CH_2I$	A	302	$\geqslant 3 \times 10^7$ [g]			nm[h]	C	300	$(4.3 \pm 0.6) \times 10^9$ [i]		nm[h]
$C_6H_5CH_2Br$	A	301	$(7.9 \pm 0.6) \times 10^8$			nm[h]	C	300	$(2.4 \pm 0.1) \times 10^9$	295	1.5×10^9 [j]
$(CH_3)_3CBr$	A	300	$(8.6 \pm 1.0) \times 10^7$	A	296	$(1.7 \pm 0.2) \times 10^8$	C	300	$(1.1 \pm 0.05) \times 10^9$	298	1.4×10^8
$CH_3CH_3CH_2Br$	A	302	$(4.6 \pm 0.3) \times 10^7$	A	295	$(2.6 \pm 0.4) \times 10^7$	C	300	$(5.4 \pm 0.1) \times 10^8$ [k]	298	3.2×10^7 [l]
C_6H_5Br	A	302	$<1 \times 10^5$			nm[h]	C	298	$(1.1 \pm 0.8) \times 10^8$		nm[h]
CCl_4	A	300	$(3.1 \pm 0.5) \times 10^8$			nm[h]	C	300	$(4.6 \pm 0.8) \times 10^9$		nm[h]
$C_6H_5CH_2Cl$	A	300	$(1.9 \pm 0.2) \times 10^6$			nm[h]	C	300	$(2.0 \pm 0.6) \times 10^7$	298	1.1×10^6
$(CH_3)_3CCl$	A	300	$<5 \times 10^4$			nm[h]	C	300	$(2.5 \pm 0.2) \times 10^6$	298	2.7×10^4

[a] Same as footnote *a*, Table 1. [b] Same as footnote *b*, Table 1. [c] Data are from ref 9. Di-*tert*-butyl peroxide/Et_3SiH 1:1 (v/v) as solvent. [d] Data from ref 11 have been normalized by multiplying by a factor of 1.7 which is the average of the ratio of the *k*'s measured for $(CH_3)_3CBr$ and for RCH_2CH_2Br by laser flash photolysis in this work and by rotating sector/competitive methods in ref 11. These *k*'s are recommended "best values". [e] Same as footnote *e*, Table 1. [f] Same as footnote *f*, Table 1. [g] Lower limit. Reactants rapidly consumed in a chain reaction. [h] Not measured. [i] Value for C_2H_5I. [j] From a competitive ESR experiment against $(CH_3)_3CBr$ reported in ref 55. Value given originally has been normalized by multiplying by 1.7. [k] Value is for $CH_3(CH_2)_4Br$. [l] Value is for $CH_3(CH_2)_5Br$.

where k_0 is the rate of radical decay in the absence of substrate and may include processes such as reaction with the solvent and the radical precursors.[31] In most of the systems studied in this work k_0 was much smaller than k_x[substrate] so that, in the absence of added substrate, the decay of the *n*-$Bu_3Ge\cdot$ or *n*-$Bu_3Sn\cdot$ radicals occurred predominantly by a second-order self-reaction.[6] Our plots of k_{exptl} vs. [substrate] usually exclude a point at [substrate] = 0, since the kinetic analysis requires that all the traces used follow first-order kinetics. In those systems in which k_x[substrate] could not be made to dominate either the decay of *n*-$Bu_3Ge\cdot$ or *n*-$Bu_3Sn\cdot$, or the formation of an adduct, only on upper limit could be put on k_x.

Rate constants measured for the addition of *n*-$Bu_3Ge\cdot$ and *n*-$Bu_3Sn\cdot$ to duroquinone, fluorenone, and benzil at ca. 300 K are listed in Table I. For comparative purposes, the rate constants previously measured[7] for the addition of the $Et_3Si\cdot$ radical to these compounds have also been listed, together with constants determined in this work for the addition of the *n*-$Bu_3Si\cdot$ radical. As would be expected, the $Et_3Si\cdot$ and *n*-$Bu_3Si\cdot$ radicals show very similar reactivity. Also included in this table are the results of kinetic measurements on the reactions, presumably additions,[25,33-39,41] of *n*-$Bu_3Ge\cdot$ with perfluoroacetic anhydride, propionaldehyde, and cyclohexanone and of *n*-$Bu_3Sn\cdot$ with cyclohexanone. An attempt to study the reaction of *n*-$Bu_3Sn\cdot$ with perfluoroacetic anhydride was frustrated by the occurrence of a fast, spontaneous reaction between the tin hydride and the anhydride.[42] Propionaldehyde and cyclohexanone were sufficiently unreactive toward *n*-$Bu_3Ge\cdot$ and cyclohexanone was sufficiently unreactive toward *n*-$Bu_3Sn\cdot$ that only an upper limit could be placed on the rate constant. Attempts to measure rate constants for reactions of *n*-$Bu_3Ge\cdot$ and *n*-$Bu_3Sn\cdot$ with acetophenone and β-phenylpropiophenone (which has a much shorter triplet lifetime, ~1 ns, than acetophenone)[43] were not successful. However, from the experimental conditions that were required in order to establish a kinetic competition with the self-terminations or the reactions with other substrates, it is clear that these additions to the carbonyl group of alkyl aryl ketones occur with $k \sim 10^6\ M^{-1}\ s^{-1}$.

Reactions with Other Unsaturated Compounds. Kinetic data obtained by method A for the reactions of *n*-$Bu_3Ge\cdot$ and *n*-$Bu_3Sn\cdot$ radicals with a variety of unsaturated compounds are listed in Table II together with data, most of which had been previously reported,[8] for the comparable reactions of $Et_3Si\cdot$ radicals. For some of the substrates listed in Table II these reactions have been shown by product studies or by EPR spectroscopy to be additions.[24,44-49] We presume that addition also occurs with all substrates for which reaction occurred at a measurable rate. An attempt to measure rate constants for the addition of *n*-$Bu_3Ge\cdot$ and *n*-$Bu_3Sn\cdot$ to phenylacetylene was unsuccessful because of complications due to signals that could not be characterized in detail.

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Reactions with Organic Halides. Kinetic data obtained by method A for halogen atom abstraction[10,11,19,24,28,44–46,50–55] by n-Bu$_3$Ge· and n-Bu$_3$Sn· radicals for several organic halides are summarized in Table III. Our previous data on the reaction of Et$_3$Si· radicals with these halides are also included, as are the "best" values calculated (vide infra) for the reaction of n-Bu$_3$Sn· with several of these halides from the original rotating sector study[10,11] and from a more recent competitive study.[55] Rapid consumption of reactants by radical chain processes was a major problem which precluded the measurement of all but a lower limit for the rate constants for the reactions of n-Bu$_3$Ge· radicals with iodomethane and 1-iodopropane (see Experimental Section). For the n-Bu$_3$Sn· reactions flow systems were employed, but only two substrates (1-bromopropane and *tert*-butyl bromide) were examined because of the large quantities of material required. Comparison of the present results for the two compounds with those of the earlier rotating sector/competitive study[11] suggests that the earlier rate constants for halogen abstraction should be increased by an average factor of $(1.4 + 2.0)/2 = 1.7$, which is close to the factor of about 2 we have noted previously for H-atom abstraction from n-Bu$_3$SnH by carbon-centered radicals.[14] A partial list of recommended "best" values for halogen abstraction by n-Bu$_3$Sn·, obtained by multiplying the original rate constants[11] by 1.7, has been included in Table III.

Full kinetic data for all the reactions studied in this work for which rate constants could be obtained are available as Suplementary Material.

Discussion

The rate constants measured in this work and reported in Tables I–III largely confirm the qualitative order of reactivities between R$_3$Si·, R$_3$Ge·, and R$_3$Sn· radicals, and for each of these radicals among a variety of substrates, that has been established from product and EPR spectroscopic studies. These reactivities are now on an absolute scale and, since many individual rate constants have been determined, it would be a fairly simple task to extend this scale to cover any other substrates of interest by standard competitive techniques.

For most substrates, whether the reaction involved is an addition to oxygen or to carbon or is a halogen abstraction, the n-Bu$_3$Ge· and n-Bu$_3$Sn· radicals have essentially equal reactivity, but are less reactive than Et$_3$Si· (or n-Bu$_3$Si·) radicals. The difference in reactivity between the germanium or tin-centered radicals and the silicon-centered radical increases as the absolute rate constants decrease, as would be expected. Similarly, the expected difference in reactivity between n-Bu$_3$Ge· and n-Bu$_3$Sn·, with the former radical more reactive than the latter, would presumably have become more apparent if rate constants had been measured for "slow" reactions.[56] In this connection, some thermochemical calculations[57] which indicate that the Me$_3$Ge–Cl and Me$_3$Ge–Br bonds (116 and 104 kcal/mol, respectively) are stronger than the analogous Me$_3$Si–X bonds (111 and 94 kcal/mol, respectively) and Me$_3$Sn–X bonds (101 and 85 kcal/mol, respectively) are inconsistent with our kinetic data for halogen-atom abstractions (see Table III). Furthermore, even the experimentally measured Me$_3$M–Me bond strengths (Me$_3$Si–Me, 84.8 ± 1.4 kcal/mol;[58] Me$_3$Ge–Me, 77.0 ± 1.9 kcal/mol;[59] Me$_3$Sn–Me, 69 ± 2 kcal/mol[60]) show a monotonic change that is perhaps more regular than would be suggested by our kinetic data for the addition of trialkylsilyl, -germyl, and -stannyl radicals to C═C double bonds (see Table II).

A few of the individual rate constants deserve some comment. Thus duroquinone and other paraquinones have been used as spin traps for group 4 (and other) metal-centered radicals.[38,39,61–65] The high rate constants found for the addition of the Si-, Ge-, and Sn-centered radicals help to explain their utility.

1,3-Cyclooctadiene is notably less reactive than the acyclic 1,3-pentadiene. This is probably due mainly to the presence of a terminal double bond in the latter compound. In addition, it has been reported that the C═C—C═C unit is not coplanar in the cyclic diene,[66] which will reduce the reactivity of this compound relative to that of planar conjugated dienes. It is also interesting to note that β-pinene with its single exocyclic double bond is actually more reactive than 1,3-cyclooctadiene toward Et$_3$Si·, though it is less reactive toward n-Bu$_3$Ge·. We presume that the addition of Et$_3$Si· to double bonds has a relatively early transition state, whereas the addition of n-Bu$_3$Ge· has a relatively late transition state. For this reason any resonance stabilization of the adduct radical will be more rate enhancing for the germyl than for the silyl radical.

Rate constants for the addition reactions of n-Bu$_3$Ge· and n-Bu$_3$Sn· (and Et$_3$Si·) radicals are rather similar to those recently reported[30] for some phenyl radical additions, e.g., 1.8×10^8 M^{-1} s^{-1} for methyl methacrylate, 1.1×10^8 M^{-1} s^{-1} for styrene, and 4.5×10^5 M^{-1} s^{-1} for benzene. However, this is not true for halogen-atom abstractions, e.g., $k = 7.8 \times 10^6$ M^{-1} s^{-1} for the phenyl/CCl$_4$ reaction and 1.1×10^6 M^{-1} s^{-1} for the phenyl/CH$_3$CH$_2$CH$_2$Br reaction. For the triethylsilyl radical we have previously suggested[9] (on the basis of the measured Arrhenius parameters) that its high reactivity toward halogen donors, particularly CCl$_4$, reflected the importance of charge separation in the transition state. The same explanation can be advanced to explain the high reactivity of n-Bu$_3$Ge· and n-Bu$_3$Sn·[67] toward CCl$_4$ and other halogen donors. The lower reactivity of phenyl may reflect the nonpolar nature of the transition state for halogen abstraction by this radical.

Triorganosilyl, -germyl, and -stannyl radicals are approximately tetrahedral and when generated from optically active precursors can yield products that are optically active and have retained the configuration of the starting material.[68] We have previously argued that the reactivity of triorganosilyl radicals is very little affected by the nature of the organic groups (alkyl or aryl) attached to the silicon, and have marshalled evidence in support of this position.[9] By assuming that triethylsilyl and (1-naphthyl)-phenylmethylsilyl radicals react with CCl$_4$ at the same rate, we could calculate from Sommer and Ulland's results[69] on the reaction of optically active (1-naphthyl)phenylmethylsilyl with CCl$_4$, that the rate constant for silyl radical inversion, k_{inv}, had a value of 6.8×10^9 M^{-1} s^{-1} at 80 °C.[9] Additional evidence that the rate constant for inversion of triorganosilyl radicals is of this general magnitude was presented.[9]

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For triorganogermyl radicals we also suggest that reactivity will be nearly the same whether alkyl or aryl groups are attached to the germanium.[70] Sakurai and Mochida[52] reported in 1971 that when (1-naphthyl)phenylmethylgermyl was generated from the optically active parent germane in the presence of CCl_4 it gave optically active germyl chloride. More recently Mochida et al.[71] have studied the variation in the optical purity of the product as a function of CCl_4 concentration. Kinetic analysis[9,71] yields $k_{trap}/k_{inv} = (0.52 \pm 0.13)\ M^{-1}$ at 80 °C, where k_{trap} is the rate constant for reaction of the germyl radical with CCl_4 at the temperature of the experiment. If at this temperature we assume a value of $5 \times 10^8\ M^{-1}\ s^{-1}$ for k_{trap} then $k_{inv} \sim 9.6 \times 10^8\ s^{-1}$. This value is somewhat less than the rate constant for the analogous silyl radical inversion at 80 °C ($6.8 \times 10^9\ s^{-1}$). If we assume that both inversions have the same pre-exponential factor, the barriers must differ by 1.4 kcal/mol.

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Registry No. n-Bu_3GeCl, 2117-36-4; n-$Bu_3Ge\cdot$, 55321-84-1; n-$Bu_3Sn\cdot$, 20763-88-6; n-Bu_3GeH, 998-39-0; n-Bu_3SnH, 688-73-3; $C_6H_5COCOC_6H_5$, 134-81-6; $[CF_3CF_2C(O)]_2O$, 356-42-3; CH_3CH_2CHO, 123-38-6; $H_2C{=}CHC{\equiv}N$, 107-13-1; $H_2C{=}C(CH_3)C(O)CH_3$, 814-78-8; $H_2C{=}CCl_2$, 75-35-4; $H_2C{=}CHC_6H_5$, 100-42-5; cis-$H_2C{=}CHCH{=}CHCH_3$, 1574-41-0; $trans$-$H_2C{=}CHCH{=}CHCH_3$, 2004-70-8; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; CH_3I, 74-88-4; $CH_3CH_2CH_2I$, 107-08-4; $C_6H_5CH_2Br$, 100-39-0; $(CH_3)_3CBr$, 507-19-7; $CH_3CH_2CH_2Br$, 106-94-5; C_6H_5Br, 108-86-1; CCl_4, 56-23-5; $C_6H_5CH_2Cl$, 100-44-7; $(CH_3)_3CCl$, 507-20-0; duroquinone, 527-17-3; fluorenone, 486-25-9; cyclohexanone, 108-94-1; 1,3-cyclooctadiene, 1700-10-3; β-pinene, 127-91-3.

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

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(70) As support for this view we note that the rate constants for H-atom abstraction by *tert*-butoxyl from n-Bu_3GeH and Ph_3GeH are equal within experimental error.[6]

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Solid-State Formation of Quinhydrones from Their Components. Use of Solid–Solid Reactions To Prepare Compounds Not Accessible from Solution

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Abstract: Selective molecular mobility provided by working with crystalline solids has been employed to prepare unsymmetrically substituted quinhydrones too unstable with respect to self-oxidation–reduction to be prepared by crystallization from solution. Reaction is carried out by grinding the solid components together with a mortar and pestle. Examination of the products with differential scanning calorimetry, X-ray powder photography, and Fourier transform infrared spectroscopy shows that the complexation reaction goes to completion under conditions in which no detectible redox reaction has occurred. The products are shown by X-ray powder photography to be formed in a microcrystalline state. The quinones employed for complex formation include 1,4-benzoquinone, its methyl and phenyl derivatives, 2,5-dimethyl-1,4-benzoquinone, and naphthoquinone. The hydroquinones are those obtained from this set of quinones by reduction. This method allows the formation of isomeric pairs of unsymmetrically substituted complexes such as benzoquinone–naphthohydroquinone and naphthoquinone–benzohydroquinone. Such isomeric complexes differ in color and have different infrared spectra and X-ray powder patterns. In cases where it is possible to prepare the complex by crystallization from solution its color, infrared spectrum, crystal structure, and other properties are identical with those of the same complex obtained by grinding the solid components together. Although the complexes formed in this way generally contain the quinone and hydroquinone in a ratio of 1:1, the complex of 2,5-dimethyl-1,4-benzoquinone with hydroquinone is composed of two hydroquinone molecules for each quinone and that of 2-methyl-1,4-benzoquinone with hydroquinone has a somewhat variable ratio of 1:1.5 to 1:2. In each of these cases the same complex is obtained when prepared by crystallization from solution; no 1:1 complex has been obtained from these pairs of reactants.

Unsymmetrically substituted quinhydrones have long been known to undergo a redox exchange reaction rapidly in solution but much less so in the solid state. For example, the unsymmetrically deuterium-labeled compound **1** and its redox isomer **2**,[1] the ^{14}C-labeled duroquinone–hydroduroquinone pair **3** and **4**,[2] and the phenylhydroquinone–p-chlorophenylbenzoquinone **5** and its redox isomer **6**[3] have been prepared as solids, each essentially free from the other, and found to be stable in the crystalline state at room temperature. Although the deuterioquinhydrones **1** and **2** had been reported[1c] to undergo slow interconversion as powders when heated in the temperature range 107–120 °C, the phenylquinhydrones **5** and **6** were not interconverted even after several

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