(ca. 10 mL/mmol of 2) was introduced slowly through a cannula. The deep red color of complex 2 was immediately discharged upon its addition to the solution of anion **1u**. The resulting mixture was then stirred at -78 °C for 30 min, the appropriate electrophilic quenching agent (E–X, Table I) (5 equiv, except for the preparation of **4y** which involved using 3 equiv of *trans*-cinnamyl bromide) added, and the mixture stirred at -78 °C for an additional 30 min. The solution was warmed to 25 °C, the solvent removed under vacuum, and the resulting residue transferred, with a minimum amount of methylene chloride, to a column of silica gel. Eluting the column with 20% methylene chloride/hexane, collection of all the yellow-orange fractions, and removal of the solvent under vacuum afforded complexes **4v,x,y** as yellow-orange substances.

$(CO)_5W[C(N(CH_3)_2)CH(Si(CH_3)_3)CH_2C(CH_3)(CH_2CH{=}CH_2)C(OCH_3)]W(CO)_5$ (4w). To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.50 g, 1.3 mmol) in 50 mL of THF at -78 °C was added 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol). After stirring for 30 min at -78 °C, chlorotrimethylsilane (0.20 mL, 1.6 mmol) was added with further stirring for 30 min. The resulting solution of $(CO)_5W[C(N(CH_3)_2)CH_2Si(CH_3)_3]$[12] (at -78 °C) was then treated with 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol) followed by slow addition (through a cannula) of a solution of **2b** (0.65 g, 1.6 mmol) in 50 mL of THF. The deep red color of **2b** was immediately discharged upon its addition to the solution of anion **1w**. The resulting solution was stirred at -78 °C for 30 min followed by the addition of allyl bromide (0.54 mL, 6.2 mmol) with continued stirring for an additional 30 min. The reaction mixture was then warmed to 25 °C, the solvent removed under vacuum, and the resulting residue transferred, with a minimum amount of methylene chloride, to a column of silica gel. Eluting the column with 20% methylene chloride/hexane, collection of all the yellow-orange fractions, and removal of the solvent under vacuum afforded **4w** (0.54 g, 47%).

$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(N(CH_3)_2)]W(CO)_5$ (4z). To a solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.50 g, 1.3 mmol) in 50 mL of THF at -78 °C was added 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol). After stirring for 30 min at -78 °C a solution of **2z** (0.51 g, 1.3 mmol) in 50 mL of THF was introduced slowly through a cannula. After the addition was complete, the mixture was stirred at -78 °C for 30 min followed by the addition of chlorotrimethylsilane (0.80 mL, 6.3 mmol). The resulting reaction mixture was stirred at -78 °C for 30 min, then warmed to 25 °C and the solvent removed under vacuum, and the resulting residue transferred, with a minimum amount of methylene chloride, to a column of silica gel. Eluting the column with 25% methylene chloride/hexane, collection of all the yellow fractions, and removal of the solvent under vacuum afforded **4z** (0.48 g, 46%) as yellow needles.

Acknowledgment. We thank the Bureau of General Research (Kansas State University) for support of this research and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer (Northern Illinois Unversity). We also wish to thank Pressure Chemical Co. for their generous gift of tungsten hexacarbonyl.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, least-squares plane results, torsion angles, bond distances and angles, and final fractional coordinates (15 pages); listings of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

The Ge–H Bond Dissociation Energies of Organogermanes. A Laser-Induced Photoacoustic Study[1]

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The Ge–H bond dissociation energies (BDE's) of several alkyl- and aryl-substituted germanium hydrides have been measured in hydrocarbon solution at room temperature by a photoacoustic technique. The BDE's of these hydrides are unaffected by alkyl substitution when compared to those for GeH_4 and are in the range of 81.6–82.6 kcal/mol. Aryl substitution leads to a slightly weakened Ge–H bond (79.2–80.2 kcal/mol) in the cases of phenyl-, diphenyl-, and triphenylgermane. In an effort to further characterize the formation, spectral and decay properties of the germyl radicals some laser flash photolysis studies were carried out. The rate constants for hydrogen abstraction by *tert*-butoxy radicals were determined by nanosecond laser flash photolysis and fell in the range $(0.7–4.4) \times 10^8$ M^{-1} s^{-1}. The aryl-substituted germyl radicals add to the aromatic rings of the germane precursor. Diphenylgermyl radical adds to diphenylgermane with a rate constant of 2.9×10^5 M^{-1} s^{-1}, while phenylgermyl radical adds to phenylgermane with a rate constant of 1.2×10^6 M^{-1} s^{-1}.

Introduction

Determination of metal–hydrogen bond dissociation energies is an area of great interest for which we have found the technique of laser-induced photoacoustic calorimetry to be extraordinarily useful in determining the bond dissociation energies of organometallic compounds not conducive to classical methods of calorimetry. Homolytic bond dissociation energies (BDE's) of organometallic compounds, which are generally derived from the heats of formation of metal-centered radicals, are rather rare since these materials are unsuitable for conventional gas-phase techniques. For example, values of BDE's of organometallic compounds of group IVB are of considerable value in understanding the chemistry of these compounds.[2] Recent work from our laboratory, directed toward uncovering the bonding characteristics in a variety

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(2) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 25.

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of organosilanes, has led to the employment of some of these compounds as useful radical-based reducing agents.[3] While it was shown that triphenylsilane functions effectively as a reducing agent for primary alkyl bromides,[3c] we also demonstrated that the novel compound tris(trimethylsilyl)silane (TTMSS) serves as an excellent free-radical reducing agent that rivals tributyltin hydride in its efficiency.[3b]

Although there is a wealth of thermochemical data on Si–H BDE's due to the pioneering work of Walsh and his colleagues,[4] this accumulated wealth of information for silicon does not extend to germanium. Ingold and coworkers have shown tri-*n*-butylgermane to be about $^{1}/_{20}$ as reactive toward primary alkyl radicals and $^{1}/_{80}$ times less reactive toward secondary alkyl radicals as the corresponding tin hydride at ambient temperatures.[5] As a result, this germane has seen use as a probe for slow alkyl radical rearrangements.[5]

Several years ago, on the basis of infrared data, McKean and co-workers reported that alkyl substitution significantly weakens both Si–H and Ge–H bonds.[6] We have found that, in the case of organosilanes, the silicon–hydrogen bond is unaffected by alkyl substitution and that aryl substitution has a very slight weakening effect,[3d] thus supporting the results of earlier work by Walsh and coworkers in this area.[4a] This is in contrast with the behavior of the carbon analogues, where the C–H BDE is very sensitive to substituent effects. The electropositivities of germanium and silicon are known to be similar,[7] and therefore, the alkyl inductive effect should not be effective in the case of germanium. This has yet to be shown conclusively, however, as only the bond dissociation energies of H_3Ge–H[8] and Me_3Ge–H[9] (82.7 and 81.2 kcal/mol, respectively) have been measured.

Our interest in this area and in the factors that moderate metal–H BDE's in group IVB metal hydrides has led us to study a variety of alkyl- and aryl-substituted germanium hydrides. We have used the technique of photoacoustic calorimetry (PAC) to probe the energy of the Ge–H bond in several organogermanes and laser flash photolysis (LFP) to study the fate of phenyl-substituted germyl radicals. Thus, we also report on results concerning the formation, decay, and spectral characterization of some of the organogermyl radicals as measured via nanosecond laser flash photolysis.

Experimental Section

General Considerations. Melting points were determined on a Kofler hot stage microscope apparatus. The ^{1}H NMR spectra were recorded on a Varian EM-360 (60 MHz) spectrometer in deuteriochloroform and are reported in parts per million downfield of tetramethylsilane. Mass spectra were recorded on a Hewlett-Packard 5970A series GC–MS instrument. Analytical VPC separations were carried out on a Hewlett-Packard 5790 gas chromatograph, equipped with a flame ionization detector and a 12 m × 0.2 mm OV-101 fused silica capillary column.

Materials. The solvents benzene (Aldrich spectrophotometric grade, 99+%) and 2,2,4-trimethylpentane (isooctane, BDH Omnisolv) were used as received in the photoacoustic calorimetry (PAC) and laser flash photolysis (LFP) experiments. Triphenylgermanium chloride and phenylgermanium chloride (Aldrich) were used as received, as were tributyl-, triethyl-, trimethyl-, and diphenylgermanium chloride (Alfa). Bis(2-methoxyethyl) ether (Fisher) was distilled from CaH_2 before use. 2-Hydroxybenzophenone was recrystallized twice from ethanol. Di-*tert*-butyl peroxide (Aldrich) was passed through a column of neutral alumina at least three times before use.

Germanes. All of the germanium hydrides were prepared from the corresponding chlorides via reduction with lithium aluminum hydride, LAH.[10,11] Typically, ca. 30 mmol of the germanium chloride was carefully added to a suspension of LAH (ca. 30 mmol) in dry ethyl ether (150 mL) in a 300-mL three-necked, round-bottomed flask equipped with a reflux condenser, argon gas inlet tube, and magnetic stirrer. The mixture was stirred from 12 to 72 h at room temperature. The ethereal portion of the mixture was decanted from the remaining LAH solids and then quenched by the slow addition of ca. 150 mL of water. The ethereal extracts were washed with water and saturated brine and then dried over magnesium sulfate and filtered, and the solvent was then distilled. The remaining clear liquids were then bulb-to-bulb distilled in vacuo (ca. 0.1–1 mmHg) to afford clear colorless products. In the case of triphenylgermane, the solid was recrystallized from pentane to afford a translucent solid.

Trimethylgermane was prepared from chlorotrimethylgermane by LAH reduction in bis(2-methoxyethyl) ether and subsequently collected in a dry ice/acetone trap (−78 °C), after which the low-boiling liquid was distilled in a manner similar to that described above.

Trimethylgermane: ^{1}H NMR δ 3.75 (m, 1 H), 0.2 (d, 9 H); MS *m/e* (intensity (*I*)) 119 (19), 117 (15), 115 (11), 107 (22), 105 (100), 104 (54), 103 (77) 102 (24), 101 (55), 100 (17), 91 (16), 89 (62), 88 (28), 87 (52), 85 (27), 75 (19), 74 (24), 73 (19), 72 (15), 70 (12).

Triethylgermane: ^{1}H NMR δ 3.71 (m, 1 H), 1.08 (m, 15 H); MS *m/e* (*I*) 161 (3), 160 (2), 133 (64), 131 (55), 105 (100), 103 (91), 101 (73), 77 (25), 75 (39), 73 (33).

Tributylgermane: ^{1}H NMR[12] δ 3.75 (m, 1 H), 1.17 (m, 27 H); MS *m/e* (*I*) 245 (1), 244 (1), 189 (55), 187 (46), 185 (31), 133 (100), 131 (78), 129 (60), 105 (18), 103 (20), 101 (18), 91 (26), 89 (31), 87 (24), 75 (12), 74 (12), 73 (12).

Phenylgermane: ^{1}H NMR δ 7.33 (m, 5 H), 4.29 (s, 3 H); MS *m/e* (*I*) 154 (64), 153 (71), 152 (100), 151 (78), 150 (75), 149 (52), 148 (28), 125 (15), 123 (17), 121 (11), 99 (29), 97 (22), 95 (16), 79 (83), 77 (39), 74 (46).

Diphenylgermane: ^{1}H NMR δ 7.43 (m, 10 H), 5.20 (s, 2 H); MS *m/e* (*I*) 229 (26), 228 (23), 227 (22), 226 (18), 225 (16), 152 (100), 151 (87), 150 (79), 149 (57), 148 (53), 147 (37), 125 (15), 99 (20), 74 (57), 72 (41), 70 (31).

Triphenylgermane: mp 40.5–41.5 °C (lit.[13] mp 41–41.5 °C); ^{1}H NMR δ 7.33 (m, 15 H), 5.61 (s, 1 H); MS *m/e* (*I*) 305 (14), 303 (9), 301 (7), 229 (34), 228 (100), 227 (86), 226 (86), 225 (48), 224 (56), 223 (27), 151 (37), 149 (30), 147 (21), 125 (6), 123 (5), 121 (4), 99 (6), 97 (4), 77 (6).

Apparatus. The technique of laser flash photolysis was used to determine the kinetics of hydrogen abstraction and radical decay and to characterize the radical spectra. Experiments were carried out with use of the pulses from a Molectron UV-24 nitrogen laser (337.1 nm, ca. 8 ns, 10 mJ/pulse). The complete apparatus and experimental technique have been described elsewhere.[14,15]

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[3] (a) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D. *J. Am. Chem. Soc.* **1987**, *109*, 5267. (b) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3541. (c) Lesage, M.; Martinho-Simões, J. A.; Griller, D. *J. Org. Chem.* **1990**, *55*, 5413. (d) Martinho-Simões, J. A.; Kanabus-Kaminska, J. M.; Griller, D. Unpublished results.

[4] (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Chapter 5, p 1.

[5] (a) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3578. (b) Lusztyk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509.

[6] McKean, D. C.; Torto, A.; Morrison, A. R. *J. Phys. Chem.* **1982**, *86*, 307.

[7] Aldred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 269.

[8] (a) Noble, P. N.; Walsh, R. *Int. J. Chem. Kinet.* **1983**, *15*, 547. (b) Almond, M. J.; Doncaster, A. M.; Noble, P. N.; Walsh, R. *J. Am. Chem. Soc.* **1982**, *104*, 4717.

[9] (a) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1977**, 446. (b) Doncaster, A. M.; Walsh, R. *J. Phys. Chem.* **1979**, *83*, 578.

[10] Kuivila, H. G.; Beumel, O. F., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1246.

[11] Stang, P. J.; White, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 5429.

[12] Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281.

[13] Lesbre, M.; Mazerolles, P.; Satge, J. In *The Organic Compounds of Germanium*; Seyferth, D., Ed.; Wiley-Interscience: New York, 1971.

[14] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

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

Where applicable, the kinetics of radical decay were studied by monitoring the change in optical density as a function of time.

Transient absorption spectra were obtained by monitoring the optical density of the radicals formed by reactions 1 and 2.

The photoacoustic apparatus has been fully described elsewhere.[16] Briefly, pulses from a Molectron UV-24 nitrogen laser (337.1 nm, ca. 8 ns, ca. 10 mJ/pulse, 2–3 Hz) were used to irradiate argon-purged solutions containing di-*tert*-butyl peroxide (2–12% v/v) and an appropriate germane (0.15–0.55 M) in benzene or isooctane. The concentrations of the germanes were chosen so that reactions 1 and 2 were complete in a time that was short compared to the response of the photoacoustic instrument. The samples flowed through standard 6.5 × 10 mm (internal dimensions) quartz luminescence flow cells (Helma 174). The photolysis gave rise to reactions 1 and 2, from which the net heat evolved produced a shock wave in the solution that propagated outward from the irradiated volume. The photoinitiated acoustic waves were detected by a piezoelectric transducer in contact with the bottom of the sample cuvette. The transducer signals were amplified, and the analog signals were relayed to a programmable digitizer/oscilloscope. To account for the variation in laser beam intensity, a beam splitter was placed in front of the sample cuvette. A fraction of the laser beam was directed to a reference cuvette/transducer/amplifier arrangement, as described above, containing ca. 10^{-4} M 2-hydroxybenzophenone in benzene. Thus, each data point obtained from the sample cuvette was "normalized" with use of the signal from the reference cuvette to correct for variations in beam intensity. Typically, 3–4 runs of 64 laser shots were averaged to produce a data point for analysis.

Photoacoustic calorimetry is a comparative technique and, as such, requires calibration before every study. 2-Hydroxybenzophenone, which dissipates 100% of the energy absorbed as heat, was used as the calibrant.[17] The apparatus was calibrated by filling the cell with optically dilute solutions of the calibrant in the chosen solvent and carrying out a photoacoustic run as described above.[18]

Two methods were used to determine the magnitude of the heat deposited during reactions 1 and 2. Method 1 involved varying the concentration of di-*tert*-butyl peroxide over a range of increasing optical density. The laser intensity remained constant throughout the experiment. The slope, a_R, obtained from a plot of normalized wave amplitudes versus the fraction of light absorbed, $1 - T$ (or $1 - 10^{-OD}$), is directly proportional to the enthalpy balance of the reaction.

In method 2, the concentration of di-*tert*-butyl peroxide remained constant and the substrate and calibrant solutions were optically matched within 1–2%. The laser beam intensity was attenuated over the range 5–100% light transmission with use of a series of neutral density filters. Two-photon absorption processes would be indicated by any departure from linearity in the plots of normalized amplitude versus relative laser intensity. Nonlinearity was not observed in these experiments.

Results and Discussion

Spectral Properties of Germanium-Centered Radicals. The spectral properties of some of the germyl radicals have been characterized previously.[19] In general, all trialkylgermyl radicals show λ_{max} at wavelengths <300 nm, while those for the arylgermyl radicals are red-shifted to wavelengths >300 nm as shown in Figure 1. The mono-, di-, and triphenylgermyl radicals are only slightly blue-shifted with respect to their corresponding carbon-centered analogues.

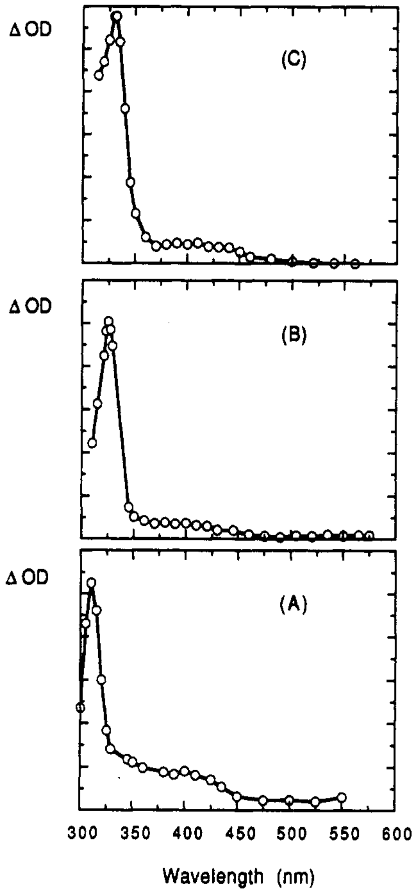

Figure 1. Absorption spectra for $PhH_2Ge^{\bullet}$ (A), $Ph_2HGe^{\bullet}$ (B), and $Ph_3Ge^{\bullet}$ (C) recorded in 2:1 di-*tert*-butyl peroxide/benzene (ca. 0.05 M germane, 19 °C, degassed with N_2). Spectra A and B were recorded with use of 337-nm excitation and spectrum C with use of 308-nm excitation. The continuous traces are artist fits only.

Table I. Spectral and Kinetic Data for Formation and Decay of Alkyl- and Aryl-Substituted Germyl Radicals

germane	radical	λ_{max} of radical, nm	k_2, M^{-1} s^{-1}	k_3, M^{-1} s^{-1}
Bu_4Ge	$Bu_3Ge(Bu\text{-}H^{\bullet})$		$(5.8 \pm 0.8) \times 10^6$	
Me_3GeH	$Me_3Ge^{\bullet}$	<300	$(6.7 \pm 0.2) \times 10^7$	*a*
Et_3GeH	$Et_3Ge^{\bullet}$	<300		*a*
Bu_3GeH	$Bu_3Ge^{\bullet}$	<300	$(9.2 \pm 1.4) \times 10^{7\,b}$	*a*
$PhGeH_3$	$PhH_2Ge^{\bullet}$	310	$(4.4 \pm 0.3) \times 10^8$	$(1.2 \pm 0.1) \times 10^6$
Ph_2GeH_2	$Ph_2HGe^{\bullet}$	325	$(1.8 \pm 0.1) \times 10^8$	$(2.9 \pm 0.2) \times 10^5$
Ph_3GeH	$Ph_3Ge^{\bullet}$	332	$(9.2 \pm 0.4) \times 10^{7\,b}$	$<1 \times 10^{5\,c}$

[a] Second-order decay.[19] [b] Reference 19. [c] Estimated.

Kinetics of Germyl Radical Formation and Decay. All experiments were carried out on deaerated samples under N_2 atmospheres. Two kinetic methods were used to determine the kinetics of hydrogen abstraction by *tert*-butoxy radicals from the germanium compounds.

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(16) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218.

(17) Allen, N. S. *Polym. Photochem.* **1983**, *3*, 167.

(18) Due to the photoreactivity of di-*tert*-butyl peroxide, the peroxide was excluded from the calibration runs. It is important to note that the photoacoustic waveform from the calibration and peroxide runs was not significantly altered nor were the times of flight for the respective waves. The time of flight of the acoustic wave was not significantly influenced by the varying levels of di-*tert*-butyl peroxide in the solution, evidence that the thermal elasticity of the solution remained virtually unchanged through the experiment. Further, in every case the results obtained in the peroxide runs remained linear even beyond 12% v/v peroxide in solution.

(19) (a) Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332. (b) Hayashi, H.; Mochida, K. *Chem. Phys. Lett.* **1983**, *101*, 307. (c) Mochida, K.; Wakasa, M.; Ishizaka, S.; Kotani, M.; Sakaguchi, Y.; Hayashi, H. *Chem. Lett.* **1985**, 1709. (d) Mochida, K.; Wakasa, M.; Nakadaira, Y.; Sakaguchi, Y.; Hayashi, H. *Organometallics* **1988**, *7*, 1869.

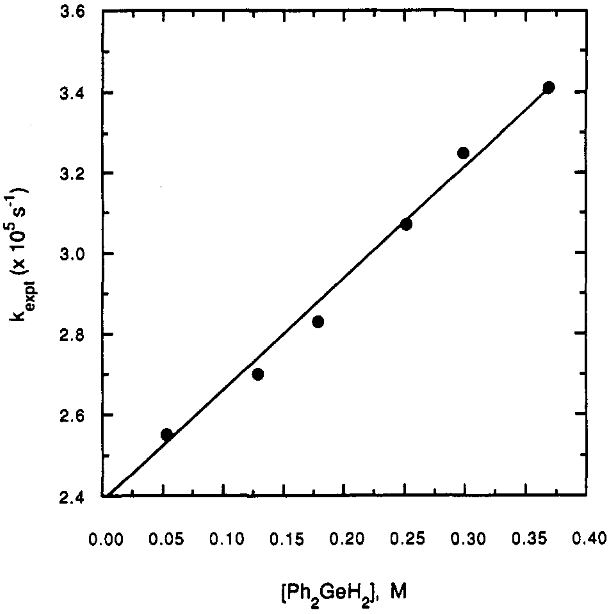


Figure 2. Reaction of Ph_2GeH_2 with $Ph_2HGe^\bullet$: plot of k_{expt} versus concentration of diphenylgermane in 3:2 di-*tert*-butyl peroxide/isooctane (20 °C, N_2 degassed, excitation wavelength 337.1 nm).

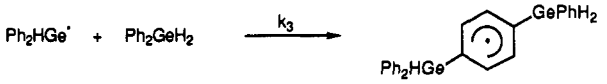
Method 1 was used in cases where the germyl radical, produced by reaction 2, exhibited a sufficient absorption,

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2\,t\text{-BuO}^\bullet \qquad (1)$$

$$2\,t\text{-BuO}^\bullet + 2R_3GeH \xrightarrow{k_2} 2\,t\text{-BuOH} + 2R_3Ge^\bullet \qquad (2)$$

enabling the time profile of its formation to be monitored directly at a number of different germane concentrations. Method 2 employed the use of a diphenylmethanol probe in cases where the absorption of the resultant germyl radical was not strong enough to directly monitor the growth profile.[15] Solutions comprised of 2:1 di-*tert*-butyl peroxide/benzene as solvent were used in both methods. Reactions of trisubstituted germanes with *tert*-butoxyl are rapid processes, k_2 falling in the range (0.7–4.4) × 10^8 M^{-1} s^{-1}. Phenyl substitution does not seem to significantly influence the rate of reaction with *tert*-butoxy radical. Rate constants for hydrogen abstraction (reactions 1 and 2) at ca. 295 K are summarized in Table I.

Decay of the aryl-substituted germyl radicals approached first-order kinetics at low concentrations of germane. The decay of these radicals deviated systematically from first-order kinetics due to competing second-order processes. The experimental first-order rate constants for radical decay, k_3, were observed to be linearly dependent on the concentration of the germane precursor (Figure 2). The experimental first-order decay can be attributed to the addition of germyl radical to an aromatic ring in the precursor (reaction 3).[20] In the case of



(3)

$Ph_2HGe^\bullet$, the rate of its addition to diphenylgermane was determined to be (2.9 ± 0.2) × 10^5 M^{-1} s^{-1}. Phenylgermyl radical adds more rapidly to the aryl groups in phenylgermane, the rate being 1.2 × 10^6 M^{-1} s^{-1}. The analogous reaction for triphenylgermyl radical was not studied, but on the basis of the rate for addition of triphenylsilyl radical to triphenylsilane (2.1 × 10^5 M^{-1} s^{-1}) we estimate the rate constant to be in the 10^4–10^5 M^{-1} s^{-1} region.

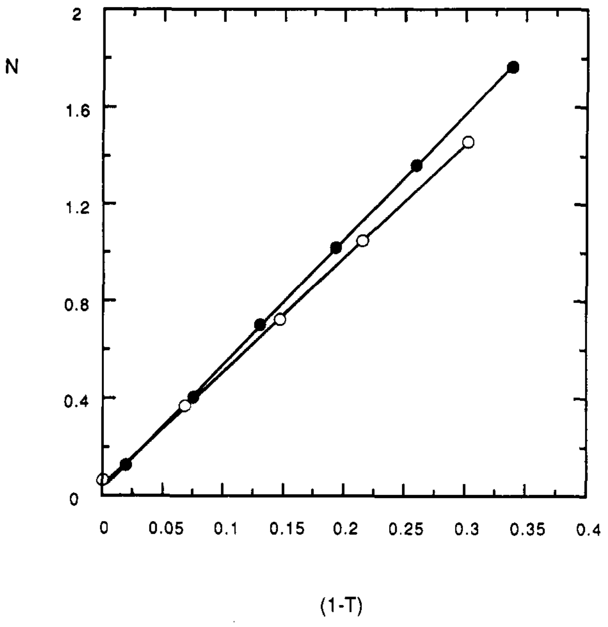


Figure 3. Plot of normalized photoacoustic response (*N*) versus light absorbed by the sample (1 – *T*): (○) *o*-hydroxybenzophenone; (●) reactions 1 and 2 (di-*tert*-butyl peroxide + triphenylgermane).

The trialkylated germyl radicals decayed with clean second-order kinetics in benzene, as reported previously.[19a]

Photoacoustic Calorimetry. In the laser-induced photoacoustic experiment the combined heats of reactions 1 and 2, $\Delta H_1 + 2\Delta H_2$ ($\Delta H_{1,2}$), is determined by measuring the heat deposited in solution. $\Delta H_{1,2}$ can be derived from the fundamental equation of photoacoustic calorimetry (eq 4), where E_{abs} is the total energy supplied to the system, E_{ST} is the energy stored or the energy that is used by the process of interest, E_L is the energy released by luminescence, and α is the fraction of the total energy dissipated as heat. The quantum yields, Φ_{ST} and Φ_L, are the efficiencies of the processes corresponding to E_{ST} and E_L, respectively. In the process of interest (eqs 1 and 2) luminescence is not important; therefore eq 4 simplifies to eq 5. E_{abs} is simply the energy associated with the 337.1-nm line of the N_2 laser, 84.8 kcal/mol, while E_{ST} represents the combined heats of reaction for reactions 1 and 2, $\Delta H_{1,2}$. The efficiency of the reaction, Φ_{ST}, is equal to the quantum yield of the photodissociation of di-*tert*-butyl peroxide (0.85 in benzene[21]).

$$E_{abs} = \alpha E_{abs} + E_{ST}\Phi_{ST} + E_L\Phi_L \qquad (4)$$

$$E_{abs} = \alpha E_{abs} + E_{ST}\Phi_{ST} \qquad (5)$$

$$\Delta H_{1,2} = 84.8(1 - \alpha)/\Phi \qquad (6)$$

Equation 6 simplifies to eq 7, bearing in mind that the energy deposited as heat, α, is the ratio of the slopes obtained from the reaction of interest, a_R, and the standard reaction, a_S (from the photolysis of 2-hydroxybenzophenone, which returns 100% of the photon energy as heat;[17] see Figure 3). Thus, the combined heats of reactions 1 and 2, $\Delta H_{1,2}$, will be equal to the photon energy less the heat deposited in solution.

$$\Delta H_{1,2} = 84.8(1 - a_R/a_S)/\Phi \qquad (7)$$

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[20] (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292. (b) Griller, D.; Marriott, P. R.; Nonhebel, D. C.; Perkins, M. J.; Wong, P. C. *J. Am. Chem. Soc.* **1981**, *103*, 7761.

[21] Martinho-Simões, J. A.; Kanabus-Kaminska, J. M.; Griller, D. Unpublished results.

Table II. Values of $\Delta H_{1,2}$ for the Reaction between Di-*tert*-butoxy Radical and Organogermanes and Bond Dissociation Energies, BDE(Ge–H)

germane	$\Delta H_{1,2}$, kcal mol^{-1}	BDE(Ge–H), kcal mol^{-1} this work	BDE(Ge–H), kcal mol^{-1} lit.
GeH_4			82.7 ± 2.4[a]
Me_3GeH	−7.0 ± 0.5	81.6 ± 0.5	81.2 ± 2.4[b]
Et_3GeH	−5.8 ± 0.8	82.3 ± 0.6	
Bu_3GeH	−5.0 ± 0.8	82.6 ± 0.6	
$PhGeH_3$	−11.8 ± 1.0	79.2 ± 0.7	
Ph_2GeH_2	−11.2 ± 1.0	79.5 ± 0.7	
Ph_3GeH	−9.9 ± 1.4	80.2 ± 0.8	

[a] Reference 8. [b] Reference 9.

To obtain bond dissociation energies, D(Ge–H), we combined eqs 8 and 9 and applied literature values for the heats of formation of t-BuOH,[22] t-BuOO-t-Bu,[23] and H•[22] and the quantum yield, Φ, which allowed determination of Ge–H bond strengths according to eq 10.

$$\Delta H_{1,2} = 2\Delta H_f(t\text{-BuOH}) + 2\Delta H_f(\text{R}^\bullet) - \Delta H_f(t\text{-BuOO-}t\text{-Bu}) - 2\Delta H_f(\text{RH}) \quad (8)$$

$$D(\text{Ge–H}) = \Delta H_f(\text{R}^\bullet) + \Delta H_f(\text{H}^\bullet) - \Delta H_f(\text{RH}) \quad (9)$$

$$\text{BDE(Ge–H)} = \Delta H_{1,2}/2 + 85.1 \quad (10)$$

In the photoacoustic experiment, it is crucial that all the heat from reactions 1 and 2, $\Delta H_{1,2}$, be released in a time that is short relative to the response of the instrument. Previous studies have shown that reactions 1 and 2 must be complete within 62 ns in order to determine $\Delta H_{1,2}$ accurately with our apparatus.[24] The concentrations of germane (0.15–0.55 M) were chosen to meet this requirement.

The BDE's of the germanium hydrides were determined in benzene or isooctane at 23 °C. The bond dissociation energies for the alkyl-substituted germanes were in the range 81.6–82.6 kcal/mol after correcting for the contribution to $\Delta H_{1,2}$ from the hydrogens located on the n-alkyl substituents. Small corrections had to be applied because, as we inferred from the work of Ingold and co-workers on tetraalkyl-substituted germanes, attack at the Ge–H bonds of the germanes by *tert*-butoxyl was the dominant but not unique mode of reaction. One can expect a small amount of attack at the methyl and/or methylene group α- and β-carbons of the germanes (reaction 11).[25] The corrections

$$t\text{-BuO}^\bullet + \text{R}_3\text{GeH} \xrightarrow{k_{11}} t\text{-BuOH} + (\text{R–H})\text{R}_2\text{GeH} \quad (11)$$

were calculated by using the ratio of rate constants k_2/k_{11} and the appropriate C–H bond strengths.[26] In each case the corrections were quite small, ≤0.5 kcal mol^{-1}, so that any imprecision in these data was of little consequence. The bond dissociation energies of these compounds were equal within experimental error in both solvents (Table II). These bond dissociation energies agree very well with the values reported by Walsh and co-workers for GeH_4 and Me_3GeH (82.7 ± 2.4 and 81.2 ± 2.4 kcal/mol,[8,9] respectively) and confirm that there is virtually no effect of alkyl substitution on the Ge–H BDE. The results reported here are also in fair agreement with the most recently reported Ge–H BDE in GeH_4 (85.5 kcal/mol), as determined by a photoionization mass spectrometric technique.[29] Results from a recent theoretical study place the Ge–H BDE at 84.8 kcal/mol.[30] Trialkylgermanes therefore behave similarly to trialkylsilanes, which is not surprising, considering the similarities in their electropositivities.[7]

The Ge–H BDE in the aryl-substituted germanes Ph_3GeH, Ph_2GeH_2, and $PhGeH_3$ were identical within experimental error (Table II). Unlike the silicon-centered derivatives, the Ge–H BDE of the aryl-substituted germanes appears little influenced by successive aryl substitution. Whereas the addition of each phenyl group through the series $PhSiH_3$ to Ph_3SiH contributes to a decrease in the Si–H BDE of ca. 2 kcal/mol,[3d] the Ge–H BDE appears less sensitive. The BDE's remained unaffected with increasing phenyl substitution through the series. The addition of germyl radicals to the phenyl rings of the germane precursors is a very slow process compared to that of H• abstraction (>100 times slower) and therefore will not contribute to $\Delta H_{1,2}$. Accordingly, the Ge–H bond dissociation energies of the aryl-substituted germanes should not be influenced by the first-order process described earlier in the discussion. The attenuation in BDE sensitivity to aryl substitution may simply result from germanium's larger size and hence less orbital overlap with the substituents than in the silane derivatives.

Summary

Alkyl and aryl substituents have virtually no influence on the bond dissociation energies of germanium hydrides. In fact, the sensitivity to these substituents appears to be attenuated somewhat in comparison to the silicon-centered analogues. The Ge–H BDE in trialkylgermanes is ca. 82 kcal/mol, while that for the aryl-substituted derivatives is ca. 80 kcal/mol.

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(22) (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. (b) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London and New York, 1986.

(23) Batt, L.; Christie, K.; Milne, R. T.; Summers, A. J. *Int. J. Chem. Kinet.* **1974**, *6*, 877.

(24) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090.

(25) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208.

(26) These bond strengths were estimated for hydrogens at carbons α and β to germanium by using C–H BDE(Me_4Si) = 99 kcal mol^{-1}[4a] and assuming that the corresponding C–H bonds in Me_4Ge are of similar value. A correction of −3 kcal mol^{-1} was allowed for the bond-weakening effect due to the β-germyl group in analogy with the β-silyl group.[27] A correction of −4 kcal mol^{-1} was used to account for the change from methyl to methylene.[28]

(27) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

(28) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(29) Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1990**, *92*, 1865.

(30) Binning, R. C., Jr.; Curtiss, L. A. *J. Chem. Phys.* **1990**, *92*, 1860.