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Kinetics and Mechanisms of the Reactions of Diaryl- and Dialkylgermylenes with Alcohols and Ethers in Solution

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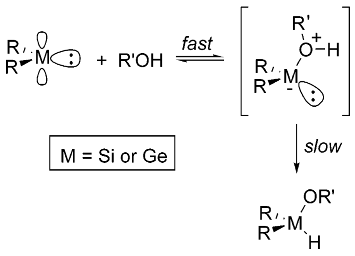
The reactions of methanol, *tert*-butanol, and THF with a series of simple germylene derivatives—dimethyl- ($GeMe_2$), diphenyl- ($GePh_2$), and dimesitylgermylene ($GeMes_2$; Mes = 2,4,6-trimethylphenyl)—have been studied in hexane solution at 25 °C by laser flash photolysis methods. The results are consistent with rapid, reversible reaction to form weakly stabilized Lewis acid−base complexes, which exhibit UV absorption maxima in the range 290−360 nm and decay with mixed order kinetics with concomitant formation of the corresponding digermene, Ge_2R_4 (R = Me, Ph, or Mes). Absolute rate constants for formation of the complexes could be measured for $GePh_2$ with all three substrates and for $GeMe_2$ with THF and were found to vary over the range $(4-10) \times 10^9\ M^{-1}\ s^{-1}$. Equilibrium constants were measured in all cases; they vary between 1.2 and 15 M^{-1} for $GeMes_2$, decreasing in the order MeOH > t-BuOH > THF, while those for $GeMe_2$ and $GePh_2$ are 2−4 orders of magnitude larger and decrease in the order THF > MeOH > t-BuOH. For a given substrate, the equilibrium constants are consistently larger for $GePh_2$ than for $GeMe_2$, reflecting the greater ability of phenyl compared to methyl substituents to stabilize negative charge at germanium in the zwitterionic complexes. In spite of the differences in the stabilities of the complexes, the rate constant for complexation with THF is almost twice as large for $GeMe_2$ than for $GePh_2$. The results indicate that the O−H insertion reaction of germylenes with alcohols proceeds via initial, reversible Lewis acid−base complexation, followed by slow proton transfer from oxygen to germanium, most likely via a catalytic route.

Introduction

Insertion into the O−H bonds of simple alcohols is one of the best known reactions of silylenes and germylenes and one of the most commonly employed trapping reactions used to demonstrate the involvement of these species as reactive intermediates in the thermal and photochemical reactions of organosilicon and organogermanium compounds.[1−5] In both cases, the reactions are thought to be initiated by Lewis acid−base complexation, followed by proton transfer from oxygen to silicon or germanium within the first-formed zwitterionic complex (eq 1). This mechanism has been inferred primarily on the basis of low-temperature spectroscopic studies, which have allowed the direct spectroscopic detection of silylene− and germylene−alcohol complexes in matrixes at 77 K,[6,7] and the results of theoretical calculations.[8−12] The same mechanism is supported by the results of fast kinetic studies of the reactions of the parent species (SiH_2[11,13] and GeH_2[14]) with water and alcohols in the gas phase, but there have not yet been any detailed mechanistic studies of the reaction in simple aryl- and alkyl-substituted derivatives by time-resolved kinetic methods in solution at ambient temperatures.



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The mechanism of silylene O−H insertions was first studied by Steele and Weber in the early 1980s, who measured primary kinetic isotope effects in the range 1.8−2.4 for the reactions of $SiMe_2$ with ethanol and *tert*-butanol by competitive product analysis methods.[15] They concluded that the reaction most likely proceeds via rapid, reversible Lewis acid−base complexation followed by rate-determining proton transfer (see eq 1), but could not rule out a concerted insertion mechanism. Later work by the same group, again based on competition kinetic methods,

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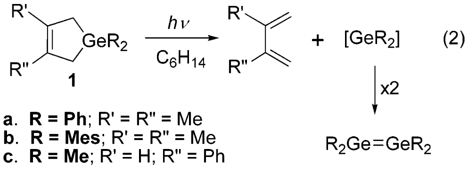
revealed a complex dependence of the relative rates of the reaction on alcohol concentration.[16] Shizuka and Das and their co-workers later reported rate constants of $k \approx 10^{10}$ M^{-1} s^{-1} for the reaction of $SiMe_2$ with various aliphatic alcohols in hydrocarbon solution at ambient temperatures, monitoring the decay of the silylene directly by laser flash photolysis.[17−19] Das and co-workers also examined the complexation of $SiMe_2$ with tetrahydrofuran (THF) in cyclohexane solution, reporting the silylene to react with the ether at close to the diffusion limit ($k_{THF} = 1.3 \times 10^{10}$ M^{-1} s^{-1} at 22 °C) to form a transient product that was assigned to the Me_2Si−THF Lewis acid−base complex on the basis of its UV/vis absorption spectrum ($\lambda_{max} = 310$ nm) and kinetic behavior.[19]

Neumann and Satge and their co-workers reported product studies of the reactions of dimethylgermylene ($GeMe_2$) with alcohols in solution and concluded that the reaction most likely proceeds via the reversible formation of a relatively long-lived germylene−alcohol complex,[20−22] in agreement with the earlier conclusions of Ando and co-workers.[7] No reliable kinetic data yet exist on the reactions of transient germylenes with alcohols in solution; while it has been variously reported that transient dialkyl and diaryl derivatives react with simple alcohols at rates that are too slow to be detected on the sub-millisecond time scale,[22−29] many of these reports are thought to be based on erroneous transient assignments.[30−33] One exception is an early time-resolved spectroscopic study of dimesitylgermylene ($GeMes_2$) from our own laboratory, in which we reported the species to exhibit no detectable signs of reactivity toward ethanol in solution.[29] More recent experience with this and other transient germylenes in solution has shown these species to be quite reactive toward various other nucleophiles[30−32] and has prompted an examination of their reactivity with simple alcohols and ethers, including a more detailed re-examination of the reactivity of $GeMes_2$ with substrates of this type.

In the present paper, we report the results of a laser flash photolysis study of the reactions of three transient germylene derivatives—diphenyl- ($GePh_2$), dimesityl- ($GeMes_2$; Mes = 2,4,6-trimethylphenyl), and dimethylgermylene ($GeMe_2$)—with methanol (MeOH), *tert*-butanol (t-BuOH), and tetrahydrofuran (THF) in hexane solution. The germylenes have been generated and monitored by laser flash photolysis of the corresponding germacyclopent-3-ene derivatives **1a−c** (eq 2), as in our previous studies of the reactivities of these transient molecules with other reagents.[30−32] Steady-state photolysis of all three of these compounds in the presence of 0.2−0.5 M MeOH has previously been shown to afford the corresponding methoxygermanes cleanly and with high quantum efficiency.[30,32] Evidence is presented herein for the formation of the corresponding Lewis acid−base complexes as the primary initial products of the reaction; the UV/vis spectra of the complexes in dilute hexane solution are reported, along with equilibrium constants and (in several cases) absolute rate constants for their formation. Absolute rate constants for reaction of the two alcohols with tetramethyl- and tetraphenyldigermene (Ge_2Me_4 and Ge_2Ph_4) have also been determined under the same conditions.



Results and Discussion

Laser flash photolysis experiments were carried out on deoxygenated solutions of **1a−c** in hexane, using the pulses from a KrF excimer laser (248 nm, ca. 25 ns, ca. 100 mJ) for excitation and a flow system to replenish the sample cell continuously between laser pulses. As reported previously,[30−32] flash photolysis of these compounds in this solvent affords promptly formed transient absorptions due to the corresponding germylene (GeR_2; λ_{max} 475−560 nm), which decays with second-order kinetics concomitantly with the growth of absorptions due to the corresponding digermene (Ge_2R_4; λ_{max} 370−440 nm). The absorption spectrum of $GePh_2$ ($\lambda_{max} = 500$ nm) overlaps significantly with that of Ge_2Ph_4 ($\lambda_{max} = 440$ nm), so kinetic analysis of the $GePh_2$ transient decays required correction of the raw absorbance data by scaled subtraction of the corresponding growth/decay profile for Ge_2Ph_4, obtained at 440 nm under identical instrumental conditions.[30,31] The spectra of $GeMe_2$ ($\lambda_{max} \approx 475$ nm) and $GeMes_2$ ($\lambda_{max} \approx 550$ nm) are sufficiently well separated from those of the corresponding digermenes (Ge_2Me_4, $\lambda_{max} = 370$ nm;[32,34] Ge_2Mes_4, $\lambda_{max} = 410$ nm[29,30,35]) that their decay kinetics could be evaluated without resorting to such corrections.

Addition of the alcohols or THF to hexane solutions of **1a−c** resulted in quenching of the germylene and digermene signals in a manner consistent with *reversible* reaction of the germylene with the added substrate, as will be described in detail below. The specific effects observed varied from system to system according to the relative magnitudes of the "forward" rate and equilibrium constants for reaction (k_Q and K_{eq}, respectively), the secondary reactivities of both the primary reaction product and the corresponding digermene toward further reaction, and the magnitude of the rate constant for dimerization of the free germylene. One feature that was common to all systems was

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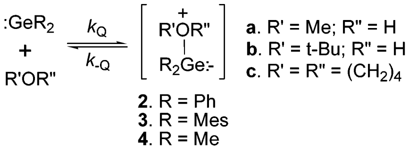
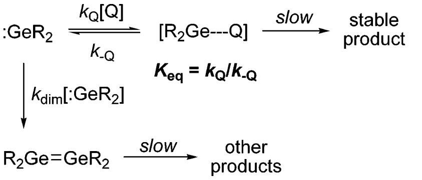
the formation of new long-lived transient absorptions in the 290−360 nm range, which increased in intensity with increasing substrate concentration and could be clearly ascribed to the primary products of reaction. These species are assigned to the corresponding Lewis acid−base complexes **2**−**4** (eq 3) on the basis of their spectroscopic and kinetic behavior (vide infra).



(3)

The general mechanistic scheme employed for analysis of the germylene transient absorption data is outlined in eq 4. We begin by noting that in order for kinetic parameters associated with reversible reaction of the germylene with a given substrate to be measurable under the conditions of our experiments, one needs to be above some threshold concentration at which the rate of approach to equilibrium significantly exceeds that of dimerization in the earliest stages of both reactions (i.e., at the end of the laser pulse). Under these conditions the decay of the germylene proceeds in two stages: a fast pseudo-first-order component due to approach to equilibrium with the primary scavenging product, and a slower second-order component due to dimerization of residual free germylene at equilibrium with the scavenging product. This threshold is determined (inter alia) by the magnitude of the dimerization rate constant, which for the three germylenes studied in this work varies between $k_{\mathrm{dim}} \approx 5 \times 10^9$ M^{-1} s^{-1} for GeMes$_2$[30] and the diffusion limit in the case of GeMe$_2$ ($k_{\mathrm{diff}} \approx 2.1 \times 10^{10}$ M^{-1} s^{-1} in hexane at 25 °C).[32] Once this condition is satisfied, then the response that is actually observed takes on one of three basic forms depending on whether K_{eq} is large (i.e., $K_{\mathrm{eq}} >$ ca. 25 000 M^{-1}), intermediate (i.e., $\sim 1000 < K_{\mathrm{eq}} < 25\,000$ M^{-1}), or small (i.e., $K_{\mathrm{eq}} <$ ca. 1000 M^{-1}), given a "forward" reaction rate constant (k_Q) on the order of ca. 10^9 M^{-1} s^{-1} or greater and typical initial germylene concentrations of 10−20 μM. The prevailing feature that distinguishes reversible reactions from irreversible ones is the *efficiency* relative to dimerization, which can be easily monitored because the dimerization reaction leads to its own detectable signal: the transient absorption due to the corresponding digermene. Qualitatively, reversible reactions are distinguishable by the fact that dimerization remains detectable even at substrate concentrations where the free germylene can no longer be detected. Scavenging efficiency can be assessed semiquantitatively by monitoring the peak intensity of the digermene signal ($\Delta A_{\mathrm{Ge_2R_4,max}}$) as a function of scavenger concentration under conditions of constant laser intensity, according to eq 5. As we have shown previously,[31,32] reversible reactions are characterized by K_{SV} values that are significantly smaller than those for irreversible ones of similar forward rate constant (k_Q). A good deal of caution is required in interpreting the results of these analyses however, because the magnitude of K_{SV} is also affected (inversely) by variations in laser intensity and (directly) by the reactivity of the digermene toward the added substrate.[31,32]



(4)

$$(\Delta A_{\mathrm{Ge_2R_4,max}})_0/(\Delta A_{\mathrm{Ge_2R_4,max}})_Q = 1 + K_{\mathrm{SV}}[\mathrm{Q}] \qquad (5)$$

The relevant kinetic equations used to analyze the germylene transient absorption data in the presence of a reversibly reacting substrate Q are given in eqs 6−8, where k_{decay} is the pseudo-first-order decay constant for approach to equilibrium with the primary scavenging product, k_Q and k_{-Q} are the forward and reverse rate constants for reaction, K_{eq} is the equilibrium constant ($=k_Q/k_{-Q}$), ΔA_0 and ΔA_t are the transient absorbance values immediately and at time = t after the laser pulse, respectively, and ΔA_{res} is the transient absorbance due to free germylene remaining after equilibrium is achieved and undergoing relatively slow decay due to the dimerization reaction. It should be noted that these equations describe the kinetics precisely only in the limit where ΔA_{res} is nondecaying, which is never strictly true. Nevertheless, we have shown previously that within certain limitations analysis of the data in this way provides reasonably accurate values of k_Q and K_{eq} for systems with K_{eq} values in the large or intermediate range.[31]

$$\Delta A_t = \Delta A_{\mathrm{res}} + (\Delta A_0 - \Delta A_{\mathrm{res}}) \exp(-k_{\mathrm{decay}}t) \qquad (6)$$

$$k_{\mathrm{decay}} = k_{-Q} + k_Q[\mathrm{Q}] \qquad (7)$$

$$\Delta A_0/\Delta A_{\mathrm{res}} = 1 + K_{\mathrm{eq}}[\mathrm{Q}] \qquad (8)$$

The simplest situation is obtained when K_{eq} is sufficiently large that the concentration of free germylene remaining at equilibrium is too small to be detected at any substrate concentration, and the germylene absorption decays from its initial value (ΔA_0) with clean pseudo-first-order kinetics to an absorbance level indistinguishable from that before the laser pulse (i.e., $\Delta A_{\mathrm{res}} \approx 0$). Only the forward rate constant for reaction (k_Q) can be determined in such cases, but it can nevertheless be determined with the same degree of precision as those for irreversible reactions. Behavior of this type is exhibited by the reaction of GePh$_2$ and GeMe$_2$ with aliphatic amines.[30−32]

The systems studied in the present work were found to fall into either the intermediate-K_{eq} regime (similar to that exhibited by the reaction of GePh$_2$ with isoprene[31]) or the small-K_{eq} regime, which we have encountered previously in a study of the complexation of dimethylstannylene (SnMe$_2$) with methanol.[36] Both k_Q and K_{eq} can be estimated with reasonable precision for systems in the intermediate-K_{eq} regime, even though the kinetic analysis is necessarily an approximate one.[31] On the other hand, for those in the small-K_{eq} regime only K_{eq} can be determined, because at concentrations high enough to cause a measurable reduction in the amount of free germylene remaining at equilibrium, the initial pseudo-first-order decay is too fast to be resolved from the laser pulse. As a result, the only effect observed upon addition of substrate is a reduction in the apparent strength of the germylene signal relative to its value in the absence of substrate; thus, at each substrate concentration the measured ΔA_0 value is actually that due to the free germylene at equilibrium with the germylene−substrate product (i.e., $\Delta A_0 = \Delta A_{\mathrm{res}}$). The equilibrium constant is then obtained from analysis of the initial germylene signal strengths according to eq 9, where $(\Delta A_0)_0$ and $(\Delta A_0)_Q$ are the initial germylene transient absorbances in the absence and presence of the substrate.

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$$(\Delta A_0)_0/(\Delta A_0)_Q = 1 + K_{eq}[Q] \qquad (9)$$

The kinetic details of the reactions of the three transient germylenes with the three oxygen-centered nucleophiles studied in this work varied quite significantly from system to system, requiring slightly different methods for analysis of the data for each of the germylenes studied. The data obtained for $GePh_2$ in the presence of both alcohols and THF allowed extraction of both the rate and equilibrium constants in all three cases, and thus will be presented first.

Diphenylgermylene. In all three cases, addition of small amounts of substrate to hexane solutions of **1a** resulted in kinetic behavior consistent with reversible scavenging in the intermediate-K_{eq} regime; that is, the germylene decays (after scaled subtraction of the underlying absorption due to Ge_2Ph_4) took on a bimodal form at "low" substrate concentrations and could be analyzed reasonably precisely according to eqs 6−8 within certain concentration ranges. The response of the digermene signals to added THF, MeOH, or t-BuOH varied with the substrate, due to differences in the secondary reactivity of the digermene toward the added reagent: $k_{MeOH} > k_{t-BuOH} \gg k_{THF}$.

The scaling factor used for correction of the raw transient absorption data for $GePh_2$ (vide supra) was determined from data recorded at 440 and 500 nm in hexane solution containing 1 mM THF, which reduces the lifetime of the germylene to ca. 145 ns but has minimal effects on the strength of the Ge_2Ph_4 signal or its growth/decay characteristics. The appropriate scaling factor was then determined from the relative intensities of the transient absorption versus time profiles for Ge_2Ph_4 at 440 and 500 nm; the procedure afforded a value for the scaling factor of 0.15, which is simply the relative extinction coefficients of the absorption due to the digermene at 500 and 440 nm. Details of the experiment are shown in the Supporting Information.

Representative growth/decay profiles for $GePh_2$ and Ge_2Ph_4 in the presence of THF are shown in Figure 1. Residual absorptions could be detected in the corrected $GePh_2$ decays at substrate concentrations up to 0.8 mM, above which they could no longer be distinguished from the pre-pulse absorbance level (Figure 1a). Rate constants for decay of the fast initial component were measurable over the 0.2−2.2 mM range in THF concentration. Figure 1b shows growth/decay profiles for Ge_2Ph_4, recorded under the same conditions as the germylene decays, which illustrates that the presence of THF has minimal effects on the yield of the digermene within this concentration range. This suggests that there are two mechanisms for formation of Ge_2Ph_4 under these conditions, one involving dimerization of free $GePh_2$ and one involving reaction of free $GePh_2$ with the primary scavenging product. In fact, the peak intensity of the Ge_2Ph_4 signal increased somewhat in the presence of very small amounts (0.05−0.2 mM) of THF, which can be attributed to a significant lengthening of the decay time of the signal in the presence of the ether. This effect is consistent with suppression of one of the possible decay channels for the digermene, most likely that involving reaction with free $GePh_2$; we presented kinetic evidence in an earlier paper that the decay of Ge_2Ph_4 in the absence of reactive scavengers proceeds via competing dimerization (on the long time scale) and reaction with free $GePh_2$ (on the short time scale).[30,31] The signal due to the digermene decreased in intensity as the THF concentration was increased further, but its formation could nevertheless still be detected in the presence of THF in concentrations in excess of 0.6 M (see Supporting Information). Presumably, the reduction in the apparent yield and lifetime of the digermene with increasing THF concentration is due to the presence of reactive impurities (such as water) in the sample of THF used in our experiments. While we made every attempt to render it anhydrous, there is no obvious reaction pathway involving the ether itself that might otherwise account for the effect.

Analysis of the germylene transient absorption data according to eqs 6−8 (see Figure 1c) afforded values for the forward rate and equilibrium constants of $k_Q = (6.3 \pm 0.6) \times 10^9$ M^{-1} s^{-1} and $K_{eq} = 23\,000 \pm 5000$ M^{-1}. A plot of the relative peak intensities of the Ge_2Ph_4 absorptions versus [THF] according to eq 5 over the 0−0.6 M concentration range afforded $K_{SV} = 6.1 \pm 0.4$ M^{-1}, which as mentioned above should be considered an upper limit of the true value. Nevertheless, the ratio K_{SV}/k_Q ($\leq$1 ns) that is defined by these data is at least 3 orders of magnitude smaller than those characteristic of formally irreversible reactions of $GePh_2$ that we have studied previously, as expected for a reversible reaction.[31] Within certain limitations, the K_{SV}/k_Q ratio provides a numeric indicator of the efficiency of a scavenging reaction relative to dimerization, and the values measured in the present work are the lowest that we have yet encountered.

Figure 2 illustrates the behavior of the transient absorptions due to $GePh_2$ and Ge_2Ph_4 in the presence of MeOH. Bimodal decay behavior was observed over a considerably broader range in substrate concentration than what was observed with THF, consistent with a significantly lower equilibrium constant for reaction. While the effects of added substrate on the germylene decay profiles are similar to those observed in the presence of THF, quenching of digermene formation by the added alcohol (as measured by the reduction in the peak signal intensities due to Ge_2Ph_4 in the presence of added alcohol) *appears* to be much more efficient than is the case with THF; a value of $K_{SV} = 660 \pm 60$ M^{-1} was obtained from a plot of the relative Ge_2Ph_4 signal intensities versus [MeOH] according to eq 5 (see Supporting Information). The greater apparent efficiency is due to secondary reaction of the digermene with MeOH, which leads to enhancements in the decay rate of the digermene signals with increasing substrate concentration and thus enhances the effect of the added substrate on the peak signal intensities. The decaying portions of the digermene growth/decay profiles (see Figure 2b) followed clean pseudo-first-order kinetics in the presence of 1−5 mM MeOH, and a plot of the decay constants (k_{decay}) versus [MeOH] according to eq 10 afforded a value of $k_Q = (1.9 \pm 0.4) \times 10^7$ M^{-1} s^{-1} for the absolute rate constant for quenching of the digermene by the alcohol. Analysis of the germylene decays according to eqs 6−8 over the 0.3−1.7 mM [MeOH] range afforded values of $k_Q = (6.1 \pm 1.1) \times 10^9$ M^{-1} s^{-1} and $K_{eq} = 3300 \pm 800$ M^{-1} (see Figure 2c).

$$k_{decay} = k_0 + k_Q[Q] \qquad (10)$$

With both THF and MeOH the effects described above were accompanied by the formation of new transient absorptions centered at 350−355 nm, which intensified with increasing concentration of added substrate. Figure 3 shows transient absorption spectra recorded in the presence of 2.1 mM THF (a) and 5 mM MeOH (b), where the lifetime of the free germylene was less than ca. 60 ns. Three spectra are shown in each case, one recorded within 50 ns after the laser pulse (the regions below 350−380 nm are obscured due to sample fluorescence), one recorded ca. 100 ns after the pulse, and another recorded ca. 3.5 μs later. In both cases, it is clear that within 100 ns after excitation the characteristic spectrum of $GePh_2$ ($\lambda_{max} = 500$ nm) is replaced by that of a second species ($\lambda_{max} = 350$−355 nm), whose subsequent decay is accompanied

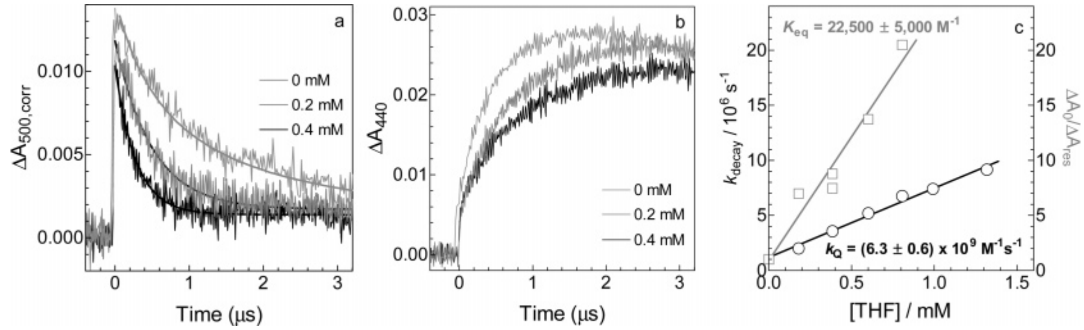


Figure 1. (a) Corrected decay profiles for $GePh_2$ in deoxygenated hexane solution containing 0−0.4 mM THF, after subtraction of the contributions due to competing absorption by Ge_2Ph_4 on the same time scale (data of (b), × 0.15). The solid lines are the best fits of the data to second- (0 mM) or first-order (0.2, 0.4 mM) kinetics. (b) Growth/decay profiles for Ge_2Ph_4 in the presence of 0−0.4 mM THF. (c) Plots of k_{decay} (○) and $\Delta A_0/\Delta A_{res}$ (□) vs [THF] for $GePh_2$.

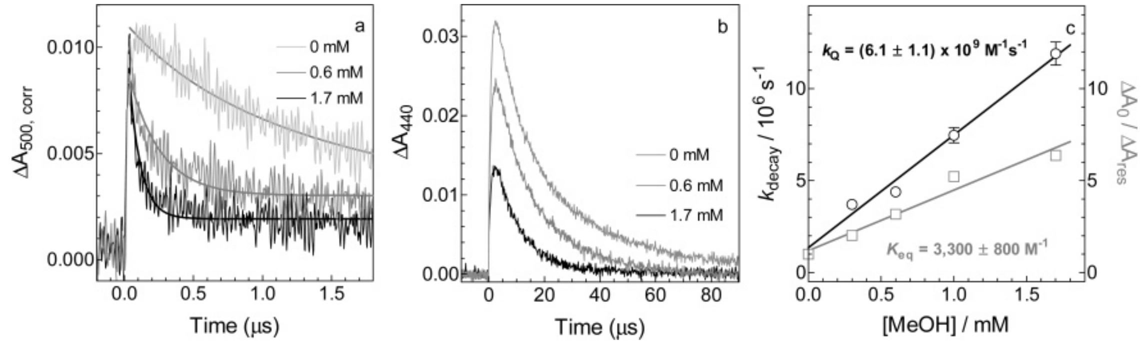


Figure 2. (a) Corrected decay profiles for $GePh_2$ in deoxygenated hexane solution containing 0−1.7 mM MeOH, after subtraction of the contributions due to competing absorption by Ge_2Ph_4 on the same time scale. The solid lines are the best fits of the data to second- (0 mM) or first-order (0.6, 1.7 mM) decay kinetics. (b) Growth/decay profiles due to Ge_2Ph_4 in the presence of 0−1.7 mM MeOH. (c) Plots of k_{decay} (○) and $\Delta A_0/\Delta A_{res}$ (□) vs [MeOH] for $GePh_2$.

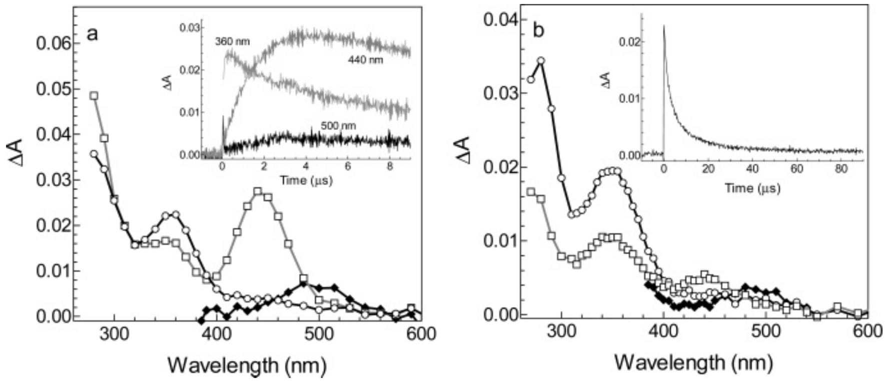


Figure 3. (a) Transient absorption spectra from laser flash photolysis of $GePh_2$ precursor **1a** in hexane containing 2.1 mM THF, recorded 16−48 ns (◆), 112−144 ns (○), and 3.36−3.47 μs (□) after the laser pulse; the inset shows transient decay profiles recorded at monitoring wavelengths of 360, 440, and 500 nm. (b) Transient absorption spectra in hexane solution containing 5.0 mM MeOH, recorded 32−48 ns (◆), 90−116 ns (○), and 3.3−3.5 μs (□) after the laser pulse; the inset shows a representative transient decay trace recorded at 350 nm.

by the formation of Ge_2Ph_4 ($\lambda_{max} = 440$ nm) on roughly the same time scale. The second-formed species are assigned to the Lewis acid−base complexes **2c** and **2a**, respectively (eq 3). The absorption maxima of these species in dilute hexane solution at ambient temperatures lie ca. 25 nm to the red of the values reported by Ando and co-workers for the complexes of $GePh_2$ with 2-methyltetrahydrofuran and ethanol in a hydrocarbon glass at 77 K.[7]

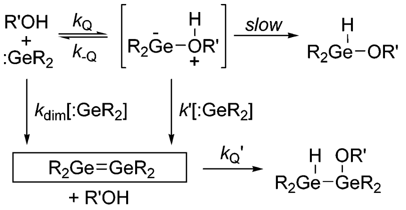
Inspection of the signals due to **2a** on shorter time scales revealed them to grow in over the first 30−60 ns after the laser pulse at low (≤5 mM) MeOH concentrations; they were unresolvable from the laser pulse at higher concentrations where the germylene's decay was also too rapid to be detected. Pseudo-first-order rate constants for the growth of the species were estimated from growth/decay profiles recorded over the 0.6−5 mM range in MeOH concentration, and a plot of k_{growth} versus [MeOH] analogous to eq 10 was linear (see Supporting Information). The slope of the plot, $k_Q = (3.7 \pm 0.3) \times 10^9$ M^{-1} s^{-1}, is in reasonable agreement with the value of k_Q estimated above from the analysis of the corrected germylene decays at 500 nm. The species decays with clean second-order kinetics under these conditions (see inset; Figure 3b), with the concomitant growth of the characteristic absorptions due to Ge_2Ph_4.

Exactly analogous behavior was observed in the presence of t-BuOH (see Supporting Information), and analysis of the data as above led to values of $k_Q = (4.8 \pm 1.6) \times 10^9$ M^{-1} s^{-1}, $K_{eq} = 800 \pm 400$ M^{-1}, and $K_{SV} = 163 \pm 16$ M^{-1}, while analysis of the digermene decays in the presence of 4−20 mM t-BuOH afforded a value of $k_Q = (2.1 \pm 0.5) \times 10^6$ M^{-1} s^{-1}. The spectrum of the Ph_2Ge−t-BuOH complex (**2b**) exhibited λ_{max} = 340 nm in hexane containing 5 mM t-BuOH; the species again decayed with kinetics similar to those of the growth of the digermene absorption. It should be noted that the plot of the $\Delta A_0/\Delta A_{res}$ data predicts an intercept significantly greater than unity. This is most likely due to overestimation of the absorbance ratios at the lower concentrations, where it is more difficult to distinguish the fast initial decay from the slower residual one than at higher substrate concentrations, where the initial decay is faster and the residual decay is slower. A value of $K_{eq} = 1000 \pm 250$ M^{-1} was obtained when the analysis was restricted to the two highest concentration data points and the unity intercept predicted by eq 6.

The data indicate there to be only slight variation in the forward rate constant for complexation of $GePh_2$ with the O-donors studied in this work, with those for complexation with THF and MeOH being slightly higher than that for t-BuOH. The complexation reaction is very fast, proceeding within a factor of 4 of the diffusion limit in hexane solution in all three cases. The main variable is the equilibrium constant, which decreases in the order $K_{THF} \approx 8K_{MeOH} \approx 25K_{t-BuOH}$ and thus appears to reflect both electronic and steric effects of substitution in the substrate on the thermodynamic stabilities of the complexes. The greater stability of the THF complex compared to those with the alcohols can be attributed to a greater degree of electronic stabilization of positive charge at oxygen and is in keeping with the higher gas-phase proton affinity of THF compared to MeOH and t-BuOH.[37] A similar analysis would predict that t-BuOH should form a stronger complex than MeOH, so the fact that it does not most likely reflects steric destabilization in the complex involving the bulkier alcohol.

The fact that the Ph_2Ge−ROH complexes decay with clean *second-order* kinetics indicates that *digermene formation* is the main mode of decay of these species under the conditions of our experiments; further reaction of the complex to yield the net insertion product proceeds much more slowly than dissociation to and subsequent formation of the digermene from the free germylene. As we concluded in the case of THF, our data indicate that the digermene is formed via two competing routes, one involving dimerization of free $GePh_2$ and one involving reaction of free $GePh_2$ with the Ph_2Ge-ROH complex (see eq 11); once formed, Ge_2Ph_4 undergoes secondary reaction with ROH to afford the 1,2-addition product.[31] In the case of THF, a third possible pathway involving dimerization of the complex can be ruled out on the basis of the fact that formation of the digermene is eventually suppressed as the substrate concentration is increased to high levels. It is more difficult to address this possibility in the cases of the alcohols, because our ability to detect the digermene at high substrate concentrations is reduced owing to its secondary reaction with the alcohols. The present data do not provide any information on the mechanism for the formation of the final (alkoxygermane) product, except that the germylene−alcohol complex is a crucial intermediate in the overall process and that its transformation to alkoxygermane via proton transfer is much slower than digermene formation under the conditions of our experiments.

Dimesitylgermylene. Very different behavior was observed in flash photolysis experiments with the $GeMes_2$ precursor (**1b**), the main feature being that addition of the alcohols or THF resulted only in successive reductions in the peak signal intensities due to the germylene with increasing substrate concentration and had no discernible effect on its decay kinetics.



(11)

In addition, the peak intensities of the digermene signals increased quite significantly upon addition of small concentrations of the three substrates (due to a lengthening of the decay time of the signal) and then decreased in the expected fashion as the concentration was increased further. As we indicated above, the increases in digermene signal strength at low substrate concentrations are consistent with suppression of one of the possible decay channels for the digermene, most likely that involving reaction with free $GeMes_2$. Considerably higher concentrations of added substrate were required in order to elicit these effects compared to those required in the experiments with $GePh_2$. Nevertheless, the observed reductions in the strength of the germylene and digermene signals were clearly coupled to the formation of new transient absorptions assignable to the Mes_2Ge−substrate complexes, the spectra of which are in reasonably good agreement with those reported by Ando et al. for the complexes of $GeMes_2$ with 2-methyltetrahydrofuran and ethanol in hydrocarbon matrixes at 77 K.[7] The results are broadly consistent with scavenging in the small-K_{eq} regime as discussed above, and so the transient absorption data for $GeMes_2$ were analyzed according to the model defined by eq 9.

Figure 4 illustrates the effects of added MeOH on the transient absorptions due to $GeMes_2$ and Ge_2Mes_4, showing (in Figure 4a) the steady reduction in signal strength for the $GeMes_2$ absorption with increasing [MeOH] and the corresponding changes in the strength of the digermene absorption (in Figure 4b), starting with an initial increase at low concentration followed by a steady decrease as the concentration is increased to higher levels. Figure 4c shows the plot of the relative initial strengths of the $GeMes_2$ signals versus [MeOH] according to eq 9. Of particular interest is the fact that the latter plot exhibits positive curvature, indicating a mixed order dependence of the intensity ratios on alcohol concentration. One possible interpretation of such a result is that $GeMes_2$ forms higher order complexes with MeOH in addition to that with the 1:1 stoichiometry. The interpretation is complicated somewhat by the fact that in hexane solution the monomeric form of methanol exists in mobile equilibrium with the hydrogen-bonded dimer and higher oligomers; the equilibrium constants are such that the concentration of the monomeric form decreases from ca. 90% of the nominal bulk concentration at 0.01 M MeOH to ca. 50% at 0.1 M at 20 °C.[38] Nevertheless, this demands that if $GeMes_2$ formed only a 1:1 complex with MeOH, then the plot of Figure 4c should exhibit negative rather than positive curvature. In any event, a quadratic fit of the data of Figure 4c defines a limiting slope of $K_{eq} = 15 \pm 6$ M^{-1} as [MeOH] → 0, as an estimate of the equilibrium constant for formation of the putative 1:1 complex with MeOH. The plot of the relative digermene peak signal intensities versus [MeOH] is similarly curved (see Supporting Information) and is characterized by a limiting slope of $K_{SV} = 3 \pm 2$ M^{-1} as [MeOH] → 0.

Similar effects were observed in flash photolysis experiments with **1b** in the presence of THF and t-BuOH, although considerably higher concentrations of added substrate were required before changes in the signal characteristics could be

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(37) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: New York, 2005; pp 259−296.

(38) Landeck, H.; Wolff, H.; Goetz, R. *J. Phys. Chem.* **1977**, *81*, 718.

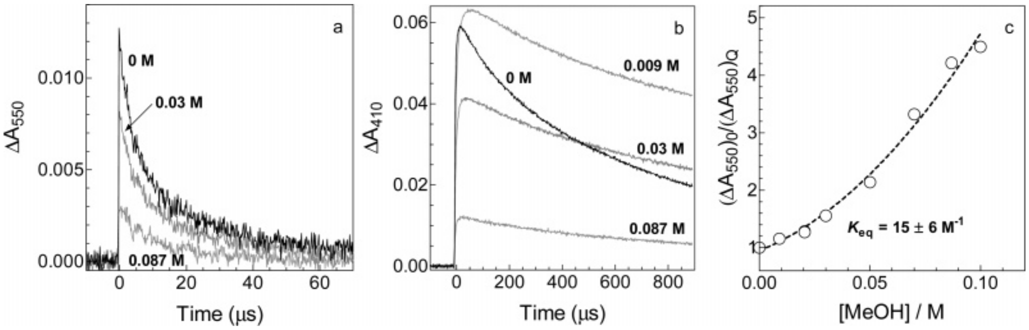

Figure 4. Growth/decay profiles for (a) $GeMes_2$ and (b) Ge_2Mes_4 in hexane containing 0−0.09 M MeOH, determined at monitoring wavelengths of 550 and 410 nm, respectively; (c) plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ for the germylene (○) signals vs [MeOH].

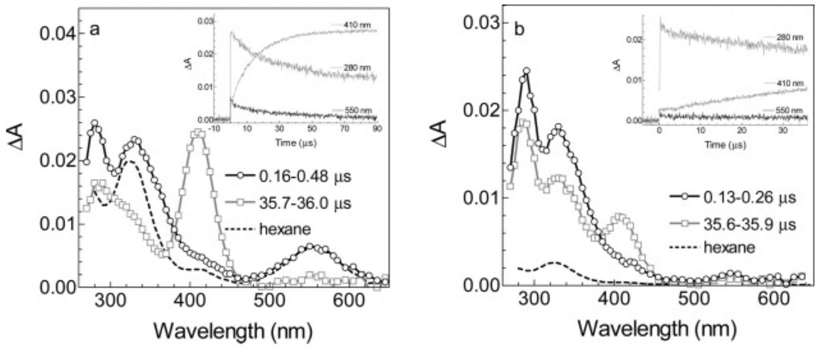

Figure 5. Transient absorption spectra recorded in hexane containing (a) 0.25 M t-BuOH, 0.16−0.48 μs (○) and 35.7−36.0 μs (□) after the laser pulse, and (b) 2.55 M t-BuOH, 0.13−0.26 μs (○) and 35.6−35.9 μs (□) after the laser pulse. The insets show decay/growth profiles recorded at monitoring wavelengths of 280, 410, and 550 nm. The spectrum of $GeMes_2$ in deoxygenated hexane (- - -), scaled to match the intensities of the 550 nm absorption band under the two sets of conditions, is also shown.

observed. Plots of the relative initial intensities of the $GeMes_2$ absorptions versus substrate concentration (eq 9) were linear in both cases and afforded values of $K_{eq} = 1.1 \pm 0.2$ and 3.7 ± 0.2 M^{-1} for THF and t-BuOH, respectively. Complete details of the data obtained for the Mes_2Ge−THF and Mes_2Ge−BuOH systems are provided in the Supporting Information. Interestingly, the K_{SV} values for all three Mes_2Ge−substrate systems are remarkably close to the corresponding K_{eq} values. We interpret this as indicating that the additional pathway for formation of the digermene that was proposed in the cases of the $GePh_2$ systems, involving reaction of the free germylene with the germylene−substrate complex, is much slower relative to that involving dimerization of the free germylene than is the case with the less hindered $GePh_2$.

Discrete absorptions assignable to the corresponding Lewis acid−base complexes (**3a**−**c**) were more difficult to detect for $GeMes_2$ in dilute hexane solution than was the case with $GePh_2$. This was found to be due to significant overlap between the $S_0 \rightarrow S_2$ transition of free $GeMes_2$ ($\lambda_{max} = 325$ nm)[30] and the $S_0 \rightarrow S_1$ transitions of the complexes, which are expected to fall in the 330−360 nm range on the basis of the spectra reported by Ando and co-workers for $GeMes_2$ in neat 2-methyltetrahydrofuran and alcohol matrixes at 77 K[7,39] and the results presented above for $GePh_2$. Nevertheless, transient spectra recorded in the presence of relatively high concentrations of MeOH and t-BuOH showed clear evidence of the presence of the respective complexes. For example, Figures 5a and 5b show transient spectra recorded at similar time delays after the laser pulse for hexane solutions of **1b** containing 0.25 and 2.5 M t-BuOH, along with the spectrum of $GeMes_2$ in hexane without added alcohol. While at low concentrations of t-BuOH (e.g., 0.25 M; Figure 5a) the 330 nm absorption might appear to be due to $GeMes_2$ alone, the spectra at higher concentrations (e.g., 2.5 M; Figure 5b) clearly show that another species is present, which exhibits absorption bands centered at $\lambda_{max} = 290$ and 330 nm.

From the value of K_{eq} that characterizes this system (~4 M^{-1}) and eq 8, the free germylene and **3b** are predicted to be present in roughly equal amounts in the presence of 0.25 M t-BuOH, and in a ratio of ca. 1:10 in the presence of 2.5 M of the alcohol. The insets in Figure 5a,b demonstrate that the complex (monitored at 280 nm) decays on a similar time scale as the decay of free $GeMes_2$ and the growth of the signal due to Ge_2Mes_4 under both sets of conditions, consistent with the free germylene and **3b** existing in mobile equilibrium and being consumed together as dimerization proceeds. Analogous behavior was observed for hexane solutions of **1b** containing 0.1 M MeOH and 1−3 M THF, data for which are included in the Supporting Information. In these two cases, spectral subtraction was required in order to extract the spectra of the corresponding complexes, because the long-wavelength bands are somewhat broader and more diffuse than is the case for the Mes_2Ge−t-BuOH complex. Nevertheless, the spectra obtained appear to be in good agreement with those reported by Ando and co-workers for the complexes of $GeMes_2$ with 2-methyltetrahydrofuran and ethanol at 77 K.[7]

While the forward rate constants for complexation (k_Q) could not be determined in these cases, we can estimate that minimum values on the order of 10^8 M^{-1} s^{-1} would be required to produce the behavior that was actually observed, given equilibrium constants in the range 1−10 M^{-1} and the maximum time resolution of our system. The true values could very well be closer to 10^9 M^{-1} s^{-1}, on the basis of the values of k_Q (=(4−6) × 10^9 M^{-1} s^{-1}) determined above for $GePh_2$ and the fact that

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[39] Ando, W.; Itoh, H.; Tsumuraya, T.; Yoshida, H. *Organometallics* **1988**, *7*, 1880.

$GeMes_2$ reacts with other nucleophiles (i.e., n-butyl amine and acetic acid) with rate constants roughly half those exhibited by $GePh_2$.[30] On the other hand, the present data indicate the equilibrium constants for reaction of $GeMes_2$ with the three substrates to be as much as 4 orders of magnitude lower than the corresponding values for $GePh_2$. The trends in K_{eq} as a function of substrate also differ for the two germylenes, with the value for THF complexation being smallest in the case of $GeMes_2$ and largest in the case of $GePh_2$. This can be attributed to a greater sensitivity of the THF complexes to steric destabilization compared to those with the alcohols, to such an extent that it overrides the greater degree of electronic stabilization of positive charge at oxygen that the second alkyl substituent in the ether would normally afford.

In contrast to one of the conclusions of our own earlier study of $GeMes_2$ in hydrocarbon solution,[29,40] the results reported here for $GeMes_2$ clearly indicate that the species reacts quite rapidly with aliphatic alcohols in solution, albeit reversibly and with such unfavorable equilibrium constants that the reaction produces no discernible effect on the decay kinetics of the germylene under the typical conditions of laser flash photolysis experiments; the signal simply grows weaker as the substrate concentration is increased until it can no longer be detected at all.

Dimethylgermylene. The reactivity of $GeMe_2$ toward the three substrates proved to be much more difficult to quantify than was the case with the diarylgermylenes, because the dialkylgermylene is a significantly weaker absorber than the aryl derivatives (hence producing weaker transient signals), dimerization is significantly faster, and the equilibrium constants proved to be significantly smaller than those of $GePh_2$. Kinetic behavior similar to that presented above for $GePh_2$ was clearly evident in the data recorded for the $Me_2Ge{-}THF$ system; the free germylene decayed with bimodal kinetics at low THF concentrations (0.2−1.1 mM) and could not be detected at all at concentrations in excess of 2.5 mM, with little accompanying effect on the peak intensities of the digermene absorptions other than a slight increase in intensity and a lengthening of the decay time. There was also a systematic drop in the initial signal intensity of the germylene absorption with increasing substrate concentration, which is due to problems of inadequate time resolution; this presented particular difficulties in the determination of the equilibrium constant. A plot of the k_{decay} values obtained from analysis of the raw germylene decay profiles over the 0.1−1.1 mM range afforded an estimate of $k_Q = (10.5 \pm 2.2) \times 10^9$ M^{-1} s^{-1} for the forward rate constant. Analysis of the $\Delta A_0/\Delta A_{res}$ versus [THF] data according to eq 8 afforded a value of $K_{eq} = 4400 \pm 900$ M^{-1} when the ΔA_0 values at each concentration were taken directly from the least-squares analyses of the decay profiles; this analysis afforded an intercept of ca. 4, however. A value of $K_{eq} = 9800 \pm 3800$ M^{-1} was obtained when the analysis was restricted to the three highest concentration data points and the unity intercept was included, and employing the ΔA_0 value obtained in the absence of added scavenger as a constant at all concentrations. We believe the higher value of K_{eq} to be the more realistic estimate. Examples of decay/growth profiles and the resulting data plots are shown in the Supporting Information.

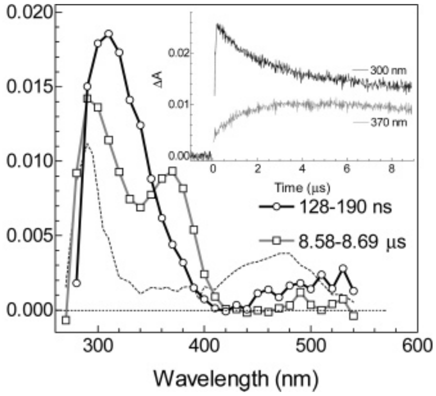

Figure 6. Transient absorption spectra of a solution of **1c** in hexane containing 15.4 mM THF, recorded 28−190 ns (○) and 8.58−8.69 μs (□) after the laser pulse. The spectrum of $GeMe_2$ in hexane solution (- - -) is included for comparison, while the inset shows transient growth/decay profiles recorded at 300 nm (bold) and 370 nm (regular).

Transient absorption spectra recorded in the presence of 15 mM THF, where the lifetime and concentration of residual free $GeMe_2$ were too small for its signal to be detected, are shown in Figure 6, along with a spectrum of $GeMe_2$ in pure hexane for purposes of comparison. The early spectrum shows evidence of new, broad absorptions centered at $\lambda_{max} = 310$ nm, which decay over the first few microseconds after excitation with the concomitant growth of the spectrum of Ge_2Me_4 ($\lambda_{max} = 370$ nm). The spectrum is assigned to the $Me_2Ge{-}THF$ Lewis acid−base complex (**4c**). The inset in the figure shows transient signals recorded at 300 and 370 nm, illustrating the decay of the 310 nm species and the concomitant growth of the signal due to Ge_2Me_4. Interestingly, the peak intensity of the Ge_2Me_4 absorption *increased* more or less continuously over the 0.2−45 mM concentration range in added THF, in contrast to the behavior observed with the arylated systems. This may be partly due to better control of reactive impurities (such as water) in the sample of THF used for the experiments with the dialkylgermylene, as this is the behavior that would actually be expected for a substrate that cannot react productively with either the germylene or its dimer. The other contributing factor is the laser intensity, which was significantly higher in this experiment than in most of the others. Saturation of the solution with air had no discernible effect on the transient decays throughout the monitoring range studied, nor on the transient spectra of Figure 6.

The effects of added MeOH and t-BuOH on the transient absorptions due to $GeMe_2$ proved to be rather more similar to what was observed with $GeMes_2$ than with $GePh_2$; complete details are provided in the Supporting Information. With MeOH as substrate, the germylene decays appeared to take on a bimodal form over the 1−4.2 mM concentration range, but the slower of the two decay components remained sufficiently fast that the approximate treatment used for estimation of k_Q and K_{eq} for the $GeMe_2{-}THF$ and $GePh_2$−substrate systems could not be applied. A fast component could not be discerned at all in transient decays recorded in the presence of higher concentrations of added alcohol; all that was observed was the ca. 2 μs decay due to residual dimerization, with an apparent initial intensity that decreased between 5 and ca. 10 mM MeOH until it could no longer be detected. An estimate of K_{eq} was thus obtained from the initial absorbance values of the slow decay component, which were estimated by eyeball extrapolation of data recorded in the presence of 3−6 mM MeOH and plotted according to eq 9 (using the value of $(\Delta A_0)_0$ from the decay recorded in the absence of MeOH). The analysis afforded an estimate of $K_{eq} = 900 \pm 60$ M^{-1} for the equilibrium constant. A value of $K_{SV} = 105 \pm 16$ M^{-1} was obtained from a plot of

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[40] The cause of the error is unknown. W.J.L. apologizes for the misdirection, particularly to his co-authors on ref 29.

the peak signal intensity ratios for Ge_2Me_4 over the 0−6 mM concentration range in this experiment; again, the intensity of the digermene signal increased slightly at the lower end of the concentration range and then decreased in the expected fashion as the concentration was increased further.

Transient absorption spectra recorded in hexane containing 54 mM MeOH at lower laser intensities showed a single transient species, which absorbs with $\lambda_{max} \approx 295$ nm and decays with complex kinetics over a time scale of several tens of microseconds (see Supporting Information). It should be noted that the species exhibits completely different temporal behavior from the long-lived absorption at ca. 290 nm that is present in the transient spectra of **1c** in pure hexane solution;[32] the latter is thought to be due to $GeMe_2$ oligomerization products and is in any event not associated with free $GeMe_2$. It is thus clear that the 295 nm species is due to the presence of the alcohol, and it is thus assigned to the $Me_2Ge{-}MeOH$ complex (**4a**).

With higher excitation laser intensities, formation of the digermene remained readily detectable in the presence of up to 45 mM MeOH, and its signals decayed with reasonably clean pseudo-first-order kinetics over the 10−45 mM range in added alcohol. A plot of the rate constants for decay of the digermene according to eq 10 was linear (see Supporting Information) and afforded a value of $k_Q = (2.7 \pm 0.8) \times 10^6$ M^{-1} s^{-1} for the rate constant for reaction of Ge_2Me_4 with MeOH. We consider the value to be in satisfactory agreement with the data reported by Mochida and co-workers for the reaction of Ge_2Me_4 with ethanol in cyclohexane, which were recorded over a much broader range in alcohol concentrations and exhibited a non-linear dependence of the digermene decay rate constant on alcohol concentration.[34]

The results obtained upon addition of t-BuOH were similar to those obtained with MeOH, except no hint of bimodal decay kinetics could be discerned in the germylene decays at any concentration within the range in which they could be detected. A value of $K_{eq} = 335 \pm 50$ M^{-1} was obtained for the equilibrium constant from analysis of the germylene absorption intensities over the 1−6 mM range in added alcohol, while $K_{SV} = 82 \pm 5$ M^{-1} was estimated from the digermene signal intensities in the 0−4 mM concentration range. A transient spectrum recorded in the presence of 8 mM t-BuOH again showed enhanced prompt absorptions in the 290−350 nm range, which decayed with the concomitant growth of the absorptions due to Ge_2Me_4 and are thus assigned to the $Me_2Ge{-}{}^tBuOH$ complex (**4b**). Representative data are shown in the Supporting Information. Addition of the alcohol also caused reductions in the lifetime of Ge_2Me_4, and a plot of k_{decay} versus [t-BuOH] over the 0.01−0.1 M range in added alcohol was linear, affording a value of $k_Q = (5 \pm 1) \times 10^5$ M^{-1} s^{-1} for the absolute rate constant for reaction of Ge_2Me_4 with t-BuOH. The value is again in satisfactory agreement with that reported for the same reaction in cyclohexane solution by Mochida and co-workers.[34]

Overview and Conclusions

The rate and equilibrium constants determined in this work for the reactions of $GePh_2$, $GeMes_2$, and $GeMe_2$ with THF, MeOH, and t-BuOH in dilute hexane solution are summarized in Table 1, along with the absorption maxima of the germylene−substrate complexes. The trends in the data can be summarized as follows.

Table 1. Absolute Rate and Equilibrium Constants for Reaction of Transient Germylenes with Alcohols and THF in Deoxygenated Hexane Solution at 25 °C and UV/Vis Absorption Maxima of the Resulting Germylene−Substrate Complexes (2−4; see eq 3) in Dilute Hexane Solution[a]

germylene		THF	MeOH	t-BuOH
$GePh_2$	$k_Q/10^9$ $M^{-1}s^{-1}$	6.3 ± 0.6	6.1 ± 1.1	4.8 ± 1.6
	K_{eq}/M^{-1}	$23\,000 \pm 5000$	3300 ± 800	1000 ± 250
	K_{SV}/M^{-1}	6.1 ± 0.4	660 ± 60	163 ± 16
	λ_{max} **2**/nm	355	350	340
$GeMes_2$	$k_Q/10^9$ M^{-1} s^{-1}	*b*	*b*	*b*
	K_{eq}/M^{-1}	1.2 ± 0.2	15 ± 6^c	3.7 ± 0.2
	K_{SV}/M^{-1}	1.9 ± 0.6	3 ± 2^c	1.6 ± 0.2
	λ_{max} **3**/nm	285, ∼360	285, ∼330	290, ∼330
$GeMe_2$	$k_Q/10^9$ M^{-1} s^{-1}	10.5 ± 2.2	*b*	*b*
	K_{eq}/M^{-1}	9800 ± 3800	900 ± 60	335 ± 50
	K_{SV}/M^{-1}	*d*	105 ± 16	82 ± 25
	λ_{max} **4**/nm	310	∼295	300

[a] Errors are reported as twice the standard deviation obtained from linear least-squares analysis of transient absorption data according to eqs 6−9; the spectra of the complexes were recorded in dilute hexane solution containing 0.01−2.5 M of the added substrate (see text), depending on the system. [b] Could not be determined. [c] Limiting slope as [MeOH] → 0. [d] Not determined.

The data indicate that reaction of all three germylenes with the three substrates proceeds rapidly and reversibly to generate the corresponding germylene−O-donor Lewis acid−base complexes, which are readily detectable as discrete transient species with lowest energy absorption maxima in the 340−355 nm range for $GePh_2$, ca. 325−360 nm for $GeMes_2$, and 295−310 nm for $GeMe_2$ in dilute hexane solution. There are generally only slight differences in the absorption maxima of the complexes of a given germylene with the three O-donors studied in this work, and the absorption maxima of the complexes with $GePh_2$ and $GeMes_2$ are similar to those reported previously in hydrocarbon matrixes at 77 K.[7] The spectrum of the $Me_2Ge{-}THF$ complex is quite similar to that reported for the $Me_2Si{-}THF$ complex under similar experimental conditions, as is the absolute rate constant for its formation as well.[19] The main difference between the silicon and germanium systems lies in the relative thermodynamic stabilities of the resulting complexes. The silylene complex enjoys much greater thermodynamic stability than the corresponding germylene complex; in contrast, the activation barriers for formation of the silylene and germylene complexes are evidently quite similar and also quite small.

Correlations have been noted previously between the positions of the absorption maxima of the complexes of silylenes and germylenes with various Lewis bases and the “strength” of the complex.[6,7] This may be valid for the complexes of a variety of substrates with a single metallylene, but the equilibrium constants and spectral data presented in this work make it clear that it is *not* valid for complexes of different germylenes with the same Lewis base. The difference between the energies of the lowest energy electronic transitions of the free and complexed germylene is significantly larger for $GeMe_2$ than $GePh_2$ in every case, in spite of the fact that the equilibrium constants are uniformly larger for the diarylgermylene. Similarly, $GeMes_2$ and $GePh_2$ exhibit spectral shifts of similar magnitudes upon complexation, in spite of the fact that the latter forms considerably stronger complexes with each of the three O-donors. Interestingly, our results suggest that $GeMes_2$ forms 1:2 and perhaps even higher order complexes with methanol, in preference to the 1:1 complexes that the data indicate to be formed with the more reactive germylenes $GePh_2$ and $GeMe_2$.

Absolute rate constants have been determined for complexation of $GePh_2$ with all three substrates and of $GeMe_2$ with THF, and vary over the narrow range $(4{-}10) \times 10^9$ M^{-1} s^{-1}; the rate constants are within a factor of 5 of the diffusion limit in hexane at 25 °C. Even though absolute rate constants could not be determined for any of the three reactions of $GeMes_2$ or for those of $GeMe_2$ with the two alcohols, it is clear that they must be of similar magnitudes to those that could actually be measured. This inference can be made on the basis of the fact that the reactions of $GeMe_2$ with a wide variety of other substrates proceed consistently a factor of ca. 2 faster than the corresponding reactions of $GePh_2$;[32] the rate constants for complexation with THF follow the same trend. There are fewer data available on which to base similar comparisons between $GeMes_2$ and $GePh_2$, but those that do exist show that $GeMes_2$ is generally only 2−3 times less reactive than $GePh_2$ under comparable conditions. In any event, the behavior observed for $GeMes_2$ in the present work requires forward rate constants for complexation of at least 10^8 M^{-1} s^{-1}.

For $GePh_2$ and $GeMe_2$, the stabilities of the germylene−O-donor complexes vary in the order THF > MeOH > t-BuOH. The variation reflects the higher Lewis basicity of the ether compared to those of the alcohols, which presumably results from a greater ability to stabilize positive charge on oxygen in the ether complex through electronic effects. In contrast, THF forms the least stable complex of the three with $GeMes_2$, presumably reflecting a greater sensitivity to steric effects on the stability of the ether complexes compared to those with the alcohols. $GePh_2$ generally forms slightly more stable complexes than $GeMe_2$, in keeping with the greater stabilization of negative charge at germanium that is afforded by phenyl compared to alkyl substituents.

The data verify inferences made previously on the basis of low-temperature spectroscopic results,[7] that the O−H insertion reaction of germylenes with alcohols proceeds via a stepwise mechanism involving the initial formation of the corresponding Lewis acid−base complex. It is clear that the second step, proton transfer from oxygen to germanium, constitutes the rate-determining step in the overall reaction pathway. The results are consistent with recent theoretical calculations for the (gas-phase) reaction of $GeMe_2$ with water, which indicate an overall activation barrier on the order of 15 kcal mol^{-1}, with formation of the initial complex proceeding exothermically by a similar amount.[9]

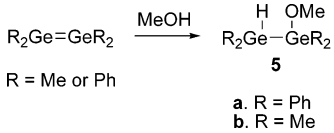
The mechanism for the proton migration/transfer process that takes the initially formed complex to the final product cannot be addressed on the basis of the results reported here, but it is nonetheless possible to define some limits. For forward rate and equilibrium constants for complexation of ca. 4×10^9 M^{-1} s^{-1} and ca. 2000 M^{-1}, respectively, the unimolecular rate constant for dissociation of the complex can be calculated to be on the order of 2×10^6 s^{-1}. The rate constant for unimolecular proton migration within the complex must clearly be at least 2 orders of magnitude slower than this, to account for the fact that the germylene−alcohol complexes are observed at all in our experiments. It seems most likely that the dominant mechanism for the second step in solution involves catalytic proton transfer, in which a second molecule of alcohol serves as the catalyst. This possibility, as well as the potential for catalysis by stronger acids and bases, will be addressed in a future paper. In dilute solution under the conditions of high-intensity laser excitation, the dominant fate of germylene−alcohol complexes is the formation of the corresponding digermene, which our data for $GeMe_2$ and $GePh_2$ indicate proceeds via two competing mechanisms: dimerization of residual free germylene in equilibrium with the complex and reaction of the complex with the free germylene. Digermene formation is eliminated when the initial concentration of the germylene is reduced or in the presence of high concentrations of alcohol, which indicates that it does not proceed via a pathway involving dimerization of the germylene−alcohol complex.

Table 2. Absolute Rate Constants for Reaction of MeOH and t-BuOH with Ge_2Me_4 and Ge_2Ph_4 in Hexane Solution at 25 °C[a]

digermene	$k_{MeOH}/10^6$ M^{-1} s^{-1}	$k_{t-BuOH}/10^6$ M^{-1} s^{-1}
Ge_2Me_4	2.7 ± 0.8	0.52 ± 0.15
Ge_2Ph_4	19 ± 4	2.1 ± 0.5

[a] Errors reported as $\pm 2\sigma$.

The absolute rate constants for reaction of Ge_2Ph_4 and Ge_2Me_4 with MeOH and t-BuOH under the conditions of our experiments are summarized in Table 2. The reaction of both digermenes with MeOH has been shown to yield the formal 1,2-addition products **5** (eq 12),[30,34] and it is reasonable to presume that the reactions with t-BuOH proceed analogously. The reactivities of the two digermenes with MeOH follow the same trend as that reported previously for reaction with amines and opposite that for addition of acetic acid.[31,32] The relative rates for both amine and alcohol addition thus correlate with the relative LUMO energies of the two digermenes,[32] consistent with either a concerted mechanism or a two-step one involving initial nucleophilic attack at germanium. The rate constants for MeOH addition are greater than those for t-BuOH addition in both cases and by similar amounts. Unlike the germylenes from which they are formed, none of the digermenes studied in this work show evidence in their UV/vis absorption spectra of significant complexation with THF.



$$R_2Ge{=}GeR_2 \xrightarrow{MeOH} R_2Ge(H){-}GeR_2(OMe) \quad (12)$$

R = Me or Ph

5

a. R = Ph
b. R = Me

Future work will explore the reactivity of transient germylene−O-donor complexes in the neat liquids, further addressing the mechanism of the O−H insertion reaction of germylenes with alcohols and exploring other facets of germylene reactivity in complexing solvents.

Experimental Section

The germacyclopentenes **1a**−**c** were synthesized and purified as described previously.[30,32] Hexanes (EMD Omnisolv) for laser flash photolysis experiments was dried by refluxing for several days under argon over sodium/potassium amalgam followed by distillation, or by passing the solvent through activated alumina (250 mesh; Sigma-Aldrich) under nitrogen using a Solvtek solvent purification system. Methanol and *tert*-butanol were both spectrophotometric grade and used as received from Sigma-Aldrich Chemical Co. Tetrahydrofuran (Caledon Reagent) was also dried by passage through activated neutral alumina (250 mesh; Aldrich) under nitrogen.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser, filled with F_2/Kr/Ne (248 nm; ∼25 ns; 100 ± 5 mJ) mixtures, and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[30] Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was between ca. 0.7 and 0.9 and were pumped continuously through a vacuum oven-dried thermostated 7 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment, using a Masterflex 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.). The glassware, sample cell, and transfer lines were dried in a vacuum oven at 65−85 °C before use. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted into the thermostated sample compartment in close proximity to the sample cell. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Transient decay and growth rate constants were calculated by nonlinear least-squares analysis of the absorbance−time profiles using the Prism 3.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (generally 4−7 points) that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

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Supporting Information Available: Representative transient decay and growth/decay profiles, time-resolved UV/vis absorption spectra, and details of kinetic analyses for each of the nine systems studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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