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Direct Detection of 1,1-Diphenylgermene in Solution and Absolute Rate Constants for Germene Trapping Reactions

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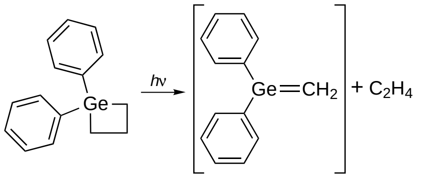
Abstract: Direct irradiation of 1,1-diphenylgermetane in hexane solution affords 1,1,3,3-tetraphenyl-1,3-digermetane in high chemical yield. Photolysis in the presence of aliphatic alcohols leads instead to the formation of the corresponding alkoxymethyldiphenylgermane. These results are consistent with the formation of 1,1-diphenylgermene as a primary photochemical product from photolysis of the germetane. Nanosecond laser flash photolysis of the compound in hexane, acetonitrile, or tetrahydrofuran gives rise to the formation of a transient, assignable to the germene on the basis of its second-order decay kinetics, UV spectrum ($\lambda_{max} = 325$ nm), and the fact that it is quenched by addition of alcohols and acetic acid. Absolute rate constants for reaction of 1,1-diphenylgermene with methanol, ethanol, 2-propanol, *tert*-butyl alcohol, acetic acid, the *O*-deuterated isotopomers, and acetone were determined in the three solvents, using the germetane as the precursor. The kinetics and mechanisms of these germene trapping reactions are discussed and compared to those of silenes.

Introduction

The chemistry of stable organometallic compounds containing a Ge═C double bond (germenes) has been extensively investigated.[1−4] Like its organosilicon homolog, the Ge═C bond is of low intrinsic thermodynamic stability, so that stable germene derivatives all contain sterically bulky substituents at both germanium and carbon. Derivatives bearing less bulky substituents are apparently highly reactive, and have been suggested as reactive intermediates in a number of thermal and photochemical reactions in organogermanium chemistry, on the basis of the products observed in the presence of various reagents included as germene traps (water, alcohols, dienes, carbonyl compounds, etc.).[3] Little *direct* evidence for their involvement as reactive intermediates has been reported, however, and the quantitative aspects of germene reactivity are largely unknown. Our recent experiences with the photochemical generation and direct detection of reactive silenes in solution[5−7] suggested that similar techniques might be used for the generation of reactive germenes in conditions under which they might be detected directly and the kinetics of their bimolecular reactions studied.

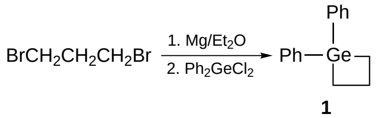
In this paper, we report the results of a study of the photochemistry of 1,1-diphenylgermetane (**1**) using steady-state and nanosecond laser flash photolysis (NLFP) techniques. Our results indicate that direct photolysis of this compound in solution leads to the formation of the highly reactive 1,1-diphenylgermene (**2**; eq 1) and ethylene, via [2 + 2]-cycloreversion in the lowest excited singlet state. NLFP techniques have allowed determination of the UV absorption spectrum of the transient germene in polar and nonpolar solvents, and absolute rate constants and kinetic deuterium isotope effects for its reaction with a series of alcohols, acetic acid, and acetone. The results allow direct comparisons to be made between the kinetics and mechanisms of the reactions of germanium−carbon double bonds with those of the corresponding silicon analogues.



1 **2** (1)

Results

1,1-Diphenylgermetane was synthesized in 91% yield by reaction of 1,3-dibromopropane with a ∼10-molar excess of ground magnesium turnings, followed by addition of diphenylgermanium dichloride (see eq 2). The method is similar to that previously reported by Bickelhaupt and co-workers for the synthesis of dialkylgermetanes,[8] but for the substitution of a large excess of (ordinary) magnesium turnings for the sublimed magnesium used in the reported procedure for preparation of



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(1) Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 241.

(2) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(3) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev. (Washington, D.C.)* **1990**, *90*, 283.

(4) Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Satgé, J. *Coord. Chem. Rev.* **1994**, *130*, 427.

(5) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5332.

(6) Leigh, W. J.; Bradaric, C. J.; Kerst, C.; Banisch, J. H. *Organometallics* **1996**, *15*, 2246.

(7) Bradaric, C. J.; Leigh, W. J. *J. Am. Chem. Soc.* **1996**, *118*, 8971.

(8) Seetz, J. W. F. L.; Van De Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1984**, *277*, 319.

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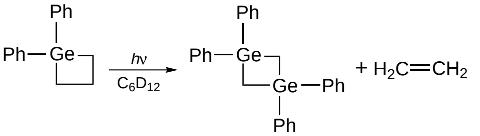
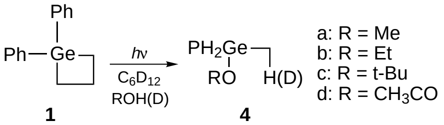
the di-Grignard reagent. The compound was purified to >99% purity by column chromatography, and identified on the basis of the usual collection of spectroscopic and analytical data (see Experimental Section).

Steady-state photolysis of deoxygenated, 0.01 M solutions of **1** in cyclohexane or cyclohexane-d_{12} led to the gradual disappearance of the germetane, and the formation of ethylene and a single germanium-containing product. The ^{1}H NMR spectrum of the crude product mixture after 10−50% conversion of **1** showed, in addition to a singlet at $\delta = 5.30$ ppm assignable to ethylene, a singlet at $\delta = 1.62$ ppm, and increased complexity in the aromatic region. Larger scale photolyses taken to higher conversions allowed isolation of the compound as a crystalline solid, which was identified as 1,1,3,3-tetraphenyl-1,3-digermetane (**3**) on the basis of spectroscopic and analytical data (eq 3). Photolysis of less pure samples of **1** under similar conditions led to the formation of ethylene, digermetane **3**, and significant amounts of a polymeric material which was not identified.



1 **3** (3)

Photolysis of **1** in hexane or C_6D_{12} containing 0.5 M methanol, ethanol, or *tert*-butyl alcohol also led in each case to the formation of ethylene and a single germanium-containing product; digermetane **3** was not formed in detectable yields in these experiments. These products were identified as the corresponding alkoxymethyldiphenylgermanes **4a**−**c** (eq 4),



1 **4** (4)

after isolation by semipreparative gas chromatography from larger scale photolyses of deoxygenated solutions of **1** in the neat alcohols, and/or by comparison to authentic samples prepared by reaction of the appropriate alcohol with methyldiphenylgermanium chloride.[9] Use of methanol-O*d* led to the formation of **4a**-*d*, in which deuterium was incorporated in the methyl group of the alkoxygermane, as illustrated in eq 4. Photolysis of a cyclohexane-d_{12} solution of **1** containing acetic acid led to the formation of a product whose NMR spectrum was consistent with acetoxygermane **4d** (eq 4), but the compound decomposed during attempts to isolate it by semipreparative GC. Photolysis of a 0.03 M solution of **1** in cyclohexane-d_{12} containing 0.07 M acetone led to the formation of polymeric material and ethylene; no other products were detectable after ~20% conversion of **1**. Experiments in which methanolic hexane solutions of **1** were photolyzed simultaneously with similar solutions of 1,1-diphenylsiletane (**5**) indicated that the quantum yield for consumption of the germetane is similar to that of the silicon analogue ($\Phi = 0.24 \pm 0.04^6$).

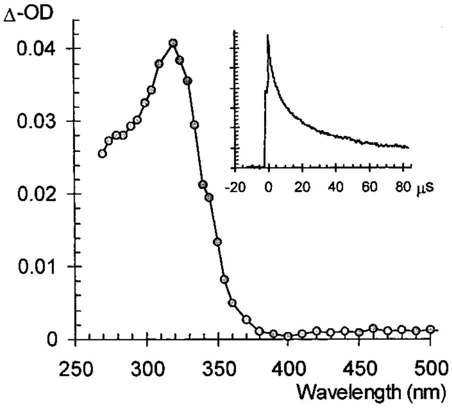


Figure 1. Time-resolved UV absorption spectra of 1,1-diphenylgermene (**2**) in deoxygenated hexane solution at 23 °C. The spectrum was recorded by laser flash photolysis of 4.4×10^{-3} M solutions of **1**, 5−10 ms after excitation (248 nm). The insert shows a typical transient decay trace, recorded at a monitoring wavelength of 325 nm.

NLFP of air-saturated 4.4×10^{-3} M solutions of **1** in hexane, acetonitrile, or tetrahydrofuran (THF), with the pulses from a KrF excimer laser (248 nm), gave rise to readily detectable transient absorptions in the 300−360 nm spectral range, which decayed over several tens of microseconds with predominantly second-order kinetics. Time-resolved absorption spectra, measured in point-by-point fashion 5−10 μs after the laser pulse, showed an absorption band with a maximum at 325 nm in all three solvents (Figure 1). The lifetime of the transient does not appear to be sensitive to the presence of oxygen or 1,3-octadiene (indicating that it is not a triplet species), but is shortened upon addition of aliphatic alcohols or acetic acid to the solution. On the basis of these observations, the transient is assigned to 1,1-diphenylgermene (**2**).

A relatively weak transient with $\lambda_{max} = 360$ nm and $\tau = 150$ ns in air-saturated solution could be detected in the presence of enough methanol or acetic acid to shorten the lifetime of **2** to less than ~100 ns. The lifetime of this transient did not change upon further additions of nucleophile, but proved to be sensitive to the presence of oxygen or aliphatic dienes. A value of $k_q = (6.1 \pm 0.8) \times 10^9$ M^{-1} s^{-1} was measured for the rate constant for quenching of the transient by 1,3-octadiene, in deoxygenated solutions of **1** in hexane containing 0.5 M MeOH. On the basis of these experiments, the 360-nm transient species is assigned to a triplet, most likely that of the germetane. However, it is difficult to rule out the possibility that it arises from excitation of small amounts of impurities present in the sample, because flash photolysis of less highly purified samples of **1** gave correspondingly greater yields of a similarly absorbing transient, superimposed on the absorptions due to **2**. Addition of 0.01 M diene to deoxygenated solutions of **1** (of any degree of purity between 95 and 99+%) shortened the lifetime of the triplet species to <20 ns but had no effect on the initial Δ-OD of the transient assigned to **2**, indicating that the triplet is not responsible for the formation of **2**.

Above certain threshold concentrations of MeOH, EtOH, 2-PrOH, or *t*-BuOH (0.005−0.02 M), the decay of germene **2** proceeds with clean pseudo-first-order kinetics, and the decay rate constant increases with increasing [ROH]. Plots of the pseudo-first-order transient decay rate constant (k_{decay}) versus alcohol concentration are approximately linear in hexane solution, as shown in Figure 2. Linear least-squares analysis of the data according to eq 5 gave acceptable fits, but with

$$k_{decay} = k_d^{o} + k_q[Q] \qquad (5)$$

negative intercepts; the apparent rate constants, given by the slopes of these plots, are summarized in Table 1. Similar experiments were carried out with MeOD and *t*-BuOD, and the

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[9] Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M. *New J. Chem.* **1989**, *13*, 389.

Table 1. Absolute Rate Constants for Reaction of 1,1-Diphenylgermene (**2**) with Alcohols, Acetic Acid, and Acetone in Air-Saturated Hexane Solution at 23 °C[a]

quencher	MeOH	EtOH	i-PrOH	*t*-BuOH	HOAc	acetone
$k_q/10^8$ M^{-1} s^{-1}	3.6 ± 0.4	2.5 ± 0.2	1.6 ± 0.2	0.35 ± 0.03	16 ± 2	<0.004 ± 0.001
k_H/k_D	1.3 ± 0.4	*b*	*b*	1.9 ± 0.3	0.9 ± 0.2	*b*

[a] From the slopes of plots of k_{decay} versus [Q] (eq 5). Errors are quoted as ±2σ. [b] Not determined.

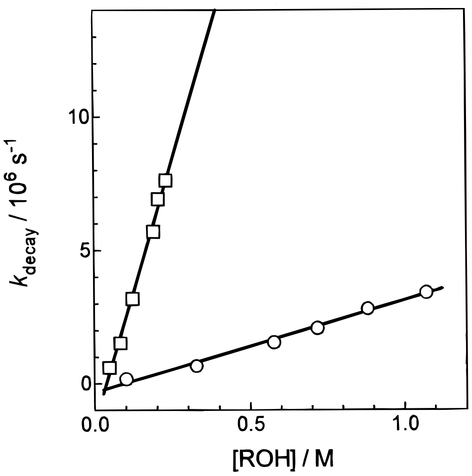


Figure 2. Plots of k_{decay} versus [ROH] for quenching of 1,1-diphenylgermene (**2**) by MeOH (□) and *t*-BuOH (○) in air-saturated hexane solution at 23 °C. The solid lines represent the least-squares fits of the data to eq 4.

results are expressed in the table as k_H/k_D values. Plots of k_{decay} versus [Q] for acetic acid and acetic acid-*d* exhibited excellent linearity and positive intercepts. Reaction of **2** with acetone was found to be too slow to be measured with our system, and only a crude upper limit for the quenching rate constant could be determined (from the lifetime of **2** in the presence of 0.23 M acetone). The rate constants obtained in these experiments are included with those for alcohol quenching in Table 1.

Addition of methanol or *t*-butanol to acetonitrile solutions of **1** also resulted in a shortening of the lifetime of germene **2**, but plots of k_{decay} versus [ROH] exhibited strong positive curvature over the ranges of alcohol concentration studied. In fact, the decay rate constants were found to fit well to the square of the alcohol concentration (r^2 > 0.99) according to eq 6. Alternative fits to a polynomial expression containing both first and second order terms in [ROH] (eq 7) gave first-order coefficients identical to zero within two standard deviations. Figure 3a shows representative plots of k_{decay} versus [ROH], for quenching of germene **2** by MeOH and *t*-BuOH in MeCN solution.

$$k_{decay} = k_d{}^o + k_{2q}[Q]^2 \tag{6}$$

$$k_{decay} = k_d{}^o + k_q[Q] + k_{2q}[Q]^2 \tag{7}$$

Plots of k_{decay} versus [MeOH] in THF solution were also curved, but curve-fitting of the data to eq 7 afforded nonzero values for both the first- and second-order terms in [ROH]. Figure 3b shows representative plots of this type for quenching of **2** by MeOH and *t*-BuOH in THF at 23 °C. Plots of k_{decay} versus [HOAc] for quenching of **2** by acetic acid in both acetonitrile and THF solution were linear, with positive intercepts. The second- and third-order rate constants (k_q and k_{2q}, respectively) obtained from the experiments in MeCN and THF solution are collected in Table 2.

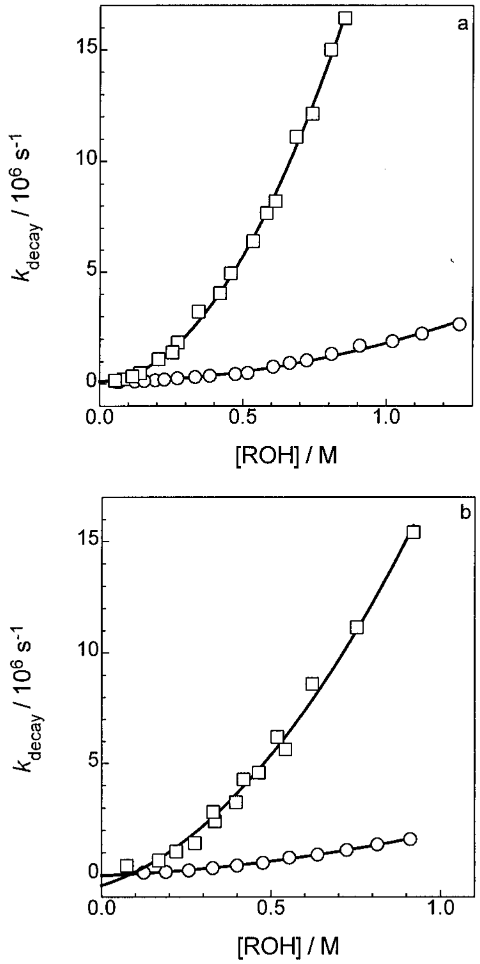


Figure 3. Plots of k_{decay} versus [ROH] for quenching of 2 at 23 °C; (a) MeOH (□) and *t*-BuOH (○) in air-saturated MeCN; (b) MeOH (□) and *t*-BuOH (○) in air-saturated THF. The solid lines represent the least-squares fit of the data to eqs 6 (a) or 7 (b).

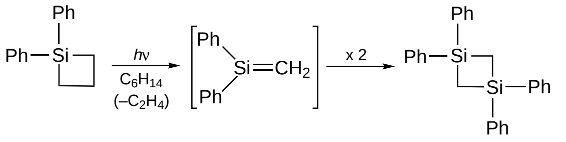
Table 2. Absolute Rate Constants for Reaction of 1,1-Diphenylgermene (**2**) with MeOH, *t*-BuOH, and HOAc in Air-Saturated Acetonitrile and Tetrahydrofuran Solution at 23 °C[a]

	quencher	MeOH	*t*-BuOH	HOAc[b]
MeCN	$k_q/10^7$ M^{-1} s^{-1}	0.03 ± 0.2[c]	0.04 ± 0.3[c]	77 ± 4
	$k_{2q}/10^7$ M^{-2} s^{-1}	2.2 ± 0.2	0.14 ± 0.02	–
THF	$k_q/10^7$ M^{-1} s^{-1}	0.5 ± 0.2	0.06 ± 0.03	18 ± 1
	$k_{2q}/10^7$ M^{-2} s^{-1}	1.4 ± 0.4	0.13 ± 0.03	–

[a] From polynomial least-squares fitting of k_{decay} versus [Q] data according to eq 7. Errors are quoted as ±2σ. [b] k_{decay} varies linearly with [HOAc] according to eq 5. [c] Indistinguishable from zero within experimental error.

Discussion

The products of direct irradiation of 1,1-diphenylgermetane (**1**), either alone or in the presence of alcohols, are consistent with the formation of 1,1-diphenylgermene (**2**) and ethylene as the primary photochemical products. This behavior is exactly analogous to that of 1,1-diphenylsiletane (**5**), which yields the head-to-tail [2+2]-dimer of 1,1-diphenylsilene (**6**; eq 8) in the



(8)

5 **6** **7**

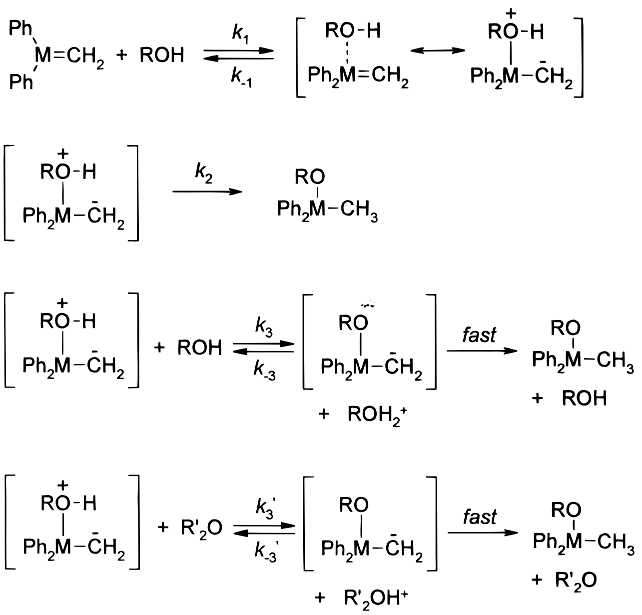
absence of silene traps,[10] or alkoxysilanes in the presence of alcohols.[5−7] These similarities between germenes and silenes are well known.[3,4] Compounds **1** and **5** both undergo [2+2]-photocycloreversion in solution with quantum yields on the order of ∼0.25, and because the initial yields of **2** and **6** (as estimated from the initial intensities of the transient absorption observed by flash photolysis) are insensitive to the presence of oxygen or diene, it can be concluded that the process is singlet-derived in both cases.[6] Thus, the photochemical behavior of 1,1-diphenylgermetane (**1**) is identical in almost every respect to that of its silicon analogue **5**.

The kinetic behavior of the 325-nm transient observed in laser flash photolysis experiments is also consistent with its assignment as **2**; it decays with predominant second-order kinetics in hexane solution (indicative of dimerization) and with pseudo-first-order kinetics in the presence of alcohols or acetic acid. The UV spectrum is indistinguishable from that of 1,1-diphenylsilene (**6**).[5] Like that of **6**, the position and breadth of the absorption band are identical in hexane and acetonitrile, but there is a slight broadening of the spectrum in THF solution. This may result from weak complexation with the solvent, but the effect is much smaller than that exhibited by the silicon analogue.[6]

As expected, 1,1-diphenylgermene reacts rapidly with aliphatic alcohols and acetic acid, although it does so significantly slower than its silicon homologue **6**.[6] The rate constants measured for **2** in hexane are mechanistically intractable (vide infra), but allow the qualitative conclusion that it exhibits the same ordering of relative reactivity as **6** toward these reagents: HOAc > MeOH > EtOH > 2-PrOH > *t*-BuOH. The ^{1}H NMR spectra of crude product mixtures from photolysis of **1** in the presence of HOAc suggest that reaction of **2** with the carboxylic acid proceeds with the same regiochemistry as the reaction with alcohols, yielding methyldiphenyl-germyl acetate (**3d**). Unfortunately however, the acetoxygermane proved to be too labile for us to isolate.

The kinetic data for reaction of **2** with MeOH and *t*-BuOH in acetonitrile suggest that the mechanism for the reaction of the germene with alcohols differs significantly from that of silenes. The latter is well understood; it is initiated by fast, reversible nucleophilic attack at silicon to form a zwitterionic complex, which collapses to alkoxysilane by two competing proton-transfer pathways—one intramolecular, and one which involves a second molecule of alcohol.[6,11,12] Although intramolecular proton-transfer is the slowest step in the sequence, it proceeds with a lower enthalpy of activation than that of reversion of the complex to starting materials. As a result, the rate constants typically show significant deuterium isotope effects, but exhibit negative overall activation energies.[7,13,14] The mechanism is shown in Scheme 1.

Scheme 1



The intervention of the pathway involving reaction of the zwitterionic complex with a second molecule of alcohol was first proposed in order to explain a dependence of alkoxysilane product distribution on bulk alcohol concentration, in the reaction of a transient cyclic silene with aliphatic alcohols.[11] Other examples of such behavior have been reported for other transient silenes as well.[6,12,15] In cases where the intracomplex proton transfer is slow enough, this mechanism also manifests itself in a quadratic dependence of the pseudo-first-order rate constant for silene decay on alcohol concentration.[12,16] For 1,1-diphenylsilene however, proton transfer by the intramolecular route is so fast that kinetic analysis reveals only the first-order dependence of k_{decay} on alcohol concentration in both acetonitrile and hexane solution.[6,7]

In fact, the kinetic data for reaction of germene **2** with alcohols and acetic acid are consistent with a mechanism very similar to that for addition of these reagents to the corresponding silene, but with one crucial difference—the proton transfer leading to conversion of the intermediate complex to alkoxygermane proceeds entirely (within our limits of detection) by the general base catalyzed route described by k_3 in Scheme 1. The base required for this step can either be the solvent (e.g., THF) or a second molecule of alcohol; in general, the two will compete for deprotonation of the complex according to their relative basicities. Deprotonation by the solvent should result in a first-order dependence of the pseudo-first-order rate constant for germene decay on [ROH], and deprotonation by ROH should result in a second-order dependence on [ROH]. Application of the equilibrium assumption for the germene−alcohol complex leads to the expression shown in eq 9 for the pseudo-first-order

$$k_{\text{decay}} = k_{\text{d}}^{\,\text{o}} + \frac{k_1[\text{ROH}]}{k_{-1}}(k_3'[\text{THF}] + k_3[\text{ROH}]) \qquad (9)$$

rate constant for decay of **2** in the presence of alcohol, where k_1, k_{-1}, k_3, and k_3' are defined in Scheme 1. THF is significantly less basic than MeOH in nonaqueous solvents;[17] thus, k_{decay} is

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(10) Jutzi, P.; Langer, P. *J. Organomet. Chem.* **1980**, *202*, 401.

(11) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986.

(12) Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1994**, *116*, 10 468.

(13) Kerst, C.; Byloos, M.; Leigh, W. J. *Can. J. Chem.* **1997**, *75*, 975.

(14) Bradaric, C. J.; Leigh, W. J. *Can. J. Chem.* **1997**, *75*, 1393.

(15) Steinmetz, M. G.; Udayakumar, B. S.; Gordon, M. S. *Organometallics* **1989**, *8*, 530.

(16) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1195.

predicted to vary with [ROH] according to eq 7 in THF, with $k_q = (k_1/k_{-1})k_3'$[THF] and $k_{2q} = (k_1/k_{-1})k_3$. In weakly basic solvents such as MeCN or hexane (where $k_3' \ll k_3$), this expression collapses to eq 6.

The results obtained for quenching of **2** by MeOH and *t*-BuOH in THF and MeCN are in excellent agreement with this mechanism, as can be seen from the data in Figure 3. In THF solution, the second-order rate coefficient k_q yields $(k_1/k_{-1})k_3' = (4 \pm 2) \times 10^5$ M^{-2} s^{-1}, which corresponds to the reaction pathway involving deprotonation of the complex by the solvent. This is a factor of ~35 lower than that involving deprotonation by a second molecule of alcohol, which is in reasonable agreement with the difference between the acid dissociation constants of protonated THF (pK_a 1.1) and $MeOH_2^+$ (pK_a 2.36) in acetonitrile solution.[17] The third-order rate constant for quenching of **2** by MeOH is slightly lower in THF than in MeCN, which could result from either weak complexation of the germene with the ether solvent or a difference in the basicity of the alcohol in the two solvents.

Although the plots of k_{decay} versus [ROH] in hexane solution are linear within experimental error, the fact that the least-squares analyses yield negative intercepts indicates that the quenching kinetics are more complex than the apparent linearity would imply. Over the alcohol concentration range employed in our kinetic experiments, both methanol and *tert*-butyl alcohol are substantially oligomerized.[18] In a plot of k_{decay} versus bulk ROH concentration, this would have the effect of linearizing the quadratic dependence on [ROH] that is predicted by the mechanism of Scheme 1. A quantitative treatment of the hexane data, taking alcohol oligomerization effects into account, is difficult to carry out without considerably more data than we have collected.

Quenching by acetic acid proceeds with strict overall second-order kinetics in all three solvents, as evidenced by the strictly linear dependences of the germene decay rate constant on [HOAc]. If addition of HOAc also involves initial complexation, as it very likely does with 1,1-diphenylsilene,[14] then the kinetics suggest that intracomplex proton transfer is much faster than is the case in the reaction with alcohols. This would be expected on the basis of the substantially greater acidity of the carboxylic acid, as well as the fact that proton transfer can proceed via a six-membered transition state if complexation occurs at the carbonyl oxygen. In hexane solution, quenching is rapid enough that a rate constant can be determined at acetic acid concentrations below that at which dimerization of the acid starts to become significant.[19] It should be noted that a mechanism for HOAc addition which involves initial protonation of the Ge═C bond cannot be ruled out on the basis of the data presented here, although we have not been able to detect additional transient species in any of our time-resolved experiments with the carboxylic acid. The substantially greater reactivity of **2** toward HOAc compared to MeOH actually makes this a reasonable possibility (**6** exhibits similar reactivities toward the two reagents[6,14]), and we are continuing to investigate it.

Nagase and co-workers have reported ab initio theoretical calculations on the addition of water to silene ($H_2Si{=}CH_2$)[20] and germene ($H_2Ge{=}CH_2$).[20,21] The calculations predict that in both cases, addition across the metal−carbon double bond involves initial complexation, followed by proton transfer from oxygen to carbon via four-membered transition states. The calculated barriers to proton transfer within the complexes are similar, suggesting that germene and silene should show similar reactivities toward nucleophilic addition. Our experimental results for alcohol additions to **2** and **6** are consistent with the intermediacy of complexes in both cases, but indicate that silene−alcohol complexes are substantially more reactive toward intramolecular proton transfer than the germanium analogues. We believe that the difference can most likely be ascribed to complexation being significantly weaker with germenes than with silenes, resulting in a lower degree of charge transfer from oxygen to the α-carbon. This would be consistent with the differences in the calculated charge distributions in germene and silene,[20] as well as with the differences in the UV absorption spectra of **2** and **6** in tetrahydrofuran solution. The spectrum of **6** is broadened considerably and slightly red-shifted in THF compared to MeCN,[6] while the spectrum of **2** in THF shows at most a very slight broadening compared to that in MeCN. These results indicate that the silene is solvated significantly more strongly than the germene by the ether solvent.

Reaction with carbonyl compounds, which generally yields 1,2-germoxetane derivatives, is one of the best known trapping reactions of stable and transient germenes.[3,4] Transient silenes are also known to react with acetone and other aliphatic ketones to yield silyl enol ethers and/or siloxetane derivatives.[22,23] The rate constants, at least for enol ether formation, are typically substantial; for example, **6** reacts with acetone with a rate constant $k \sim 3 \times 10^8$ M^{-1} s^{-1} in hexane at 23 °C.[5] We were thus surprised to find that no reaction between germene **2** and acetone could be detected by steady-state or flash photolysis methods. Because recent results indicate that the reaction of silenes with acetone is also initiated by complex formation,[24] it is possible that the much-reduced reactivity of **2** with acetone is due to similar factors as those proposed above for alcohol addition. The weaker complex formed in the germene case does not provide enough negative charge density at the germenic carbon to allow for rapid transfer of the weakly acidic α-proton.

Summary and Conclusions

The transient 1,1-diphenylgermene (**2**) can be generated and detected in solution by laser flash photolysis of 1,1-diphenylgermetane (**1**). The germene undergoes head-to-tail [2+2]-dimerization in hexane solution, or can be trapped by aliphatic alcohols as the corresponding alkoxymethyldiphenylgermanes. Kinetic evidence suggests that this reaction proceeds by a mechanism involving the initial formation of a germene−alcohol complex, as is the case with alcohol additions to silenes. Silene−alcohol complexes collapse to product by rapid intramolecular proton transfer, as well as by an intermolecular general base-catalyzed process which usually becomes important only at relatively high alcohol concentrations. In contrast, proton transfer in 1,1-diphenylgermene−alcohol complexes appears to proceed only by the general base-catalyzed pathway. This involves a second molecule of alcohol in hexane or acetonitrile, in addition to the solvent in more basic media like THF. If this mechanism is correct, then further analogy with silene chemistry[6,11,12,15] would predict that the addition of alcohols and water to germenes should proceed nonstereoselectively or perhaps even with predominant anti-stereochem-

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(17) Izutsu, K. *Acid−base dissociation constants in dipolar aprotic solvents. IUPAC Chemical Data Series #35*; Blackwell Scientific Publications: Oxford, 1990; pp 17-35.

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

(19) Fujii, Y.; Yamada, H.; Mizuta, M. *J. Phys. Chem.* **1988**, *92*, 6768.

(20) Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H. J., Schaefer, H. F., Morokuma, K., Eds.; D. Reidel: Dordrecht, 1986; pp 249−267.

(21) Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 324.

(22) Raabe, G.; Michl, J. *Chem. Rev. (Washington, D.C.)* **1985**, *85*, 419.

(23) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

(24) Bradaric, C. J.; Leigh, W. J. *Organometallics* **1998**, in press.

istry. This and other aspects of the chemistry of germene reactive intermediates are under continued investigation in our laboratory.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC200 or DRX500 NMR spectrometers in deuterated chloroform solution and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Perkin-Elmer Lambda 9 spectrometers. Low-resolution mass spectra and GC−MS analyses were determined using a Hewlett-Packard 5890 gas chromatograph equipped with an HP-5971A mass-selective detector and a DB-5 fused silica capillary column (30 m × 0.25 mm; Chromatographic Specialties, Inc.). High-resolution desorption electron impact (DEI) and chemical ionization (CI) mass spectra and exact masses were recorded on a VGH ZABE mass spectrometer. Exact masses employed a mass of 12.000000 for carbon. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). Elemental analyses were performed by Galbraith Laboratories Inc.

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396A recording integrator, conventional heated splitless injector, and a DB-1 fused silica capillary column (15 m × 0.20 mm; Chromatographic Specialties, Inc.). Semipreparative GC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector, and a 6 ft × 0.25 in. stainless steel OV-101 packed column (Chromatographic Specialties Inc.). Radial chromatographic separations employed a Chromatotron (Harrison Research, Inc.), 2- or 4-mm silica gel 60 thick-layer plates, and hexane/ethyl acetate mixtures as eluant.

Acetonitrile (Caledon Reagent) was refluxed over calcium hydride (Fisher) for several days and distilled under dry nitrogen. Hexane (Caledon Reagent) was stirred for several days over concentrated sulfuric acid, washed several times with water, washed once with saturated aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and distilled from sodium. Tetrahydrofuran (BDH Omnisolv) was refluxed for several days over sodium under nitrogen and distilled. Methanol, 2-propanol, *tert*-butanol (HPLC grade), 1,3-octadiene, and 1,3-dibromopropane were used as received from Aldrich Chemical Co. Absolute ethanol was predried with calcium hydride, distilled from magnesium under nitrogen, and stored over 3 Å molecular sieves. Benzene (Caledon) was distilled from sodium. Deuterated materials were used as received from Cambridge Isotope Labs. Diphenylgermanium dichloride was used as received from Gelest, Inc.

1,1-Diphenylgermetane (**1**) was prepared by a modification of the method of Bickelhaupt and co-workers.[8] Freshly ground magnesium turnings (45 g, 1.85 g-atom) and anhydrous ether (300 mL) were placed in a flame-dried, two-neck, 500 mL round-bottom flask fitted with a condenser and addition funnel. A solution of 1,3-dibromopropane (26.0 g, 0.129 mol) in anhydrous ether (40 mL) was added dropwise with vigorous stirring over a period of 4 h, and then left to stir overnight at room temperature. Diphenylgermanium dichloride (5.50 g, 0.0185 mol) was then added rapidly with a syringe and the mixture was left to stir for a further 8 h. The reaction mixture was decanted into a large flask, placed in an ice bath, and slowly quenched with saturated aqueous ammonium chloride (200 mL). The organic layer was separated and washed sequentially with water, 5% sodium bicarbonate, and water, and then dried with anhydrous magnesium sulfate. The solvent was removed on the rotary evaporator to yield a slightly yellow oil. Purification was accomplished using silica gel column chromatography with hexane as the eluting solvent, affording the product as a colorless oil (4.58 g, 0.0168 mol, 91%) in >99% purity. It was identified as 1,1-diphenylgermetane (**1**) on the basis of the following spectroscopic data: ^{1}H NMR $\delta = 1.96$ (t, 4H), 2.40 (m, 2H), 7.37−7.41 (m, 6H), 7.56−7.61 (m, 4H); ^{13}C NMR $\delta = 20.45$, 21.46, 128.29, 129.07, 134.01, 138.81; IR (neat), 3067.2 (s), 2926.3 (s), 1952.6 (w), 1817.1 (w), 1483.1 (m), 1430.5 (s), 1303.5 (m), 1262.0 (w), 1182.0 (w), 1091.1 (s), 843.2 (s), 788.7 (s); MS (EI) *m/z* (*I*) = 270 (5), 242 (5), 227 (7), 151 (8), 84 (20); [NH$_3$-CI], *m/z* (*I*) = 288 (95), 269 (15), 244 (8), 210 (100), 181 (10), 162 (10), 137 (12), 113 (13), 78 (45), 52 (82); exact mass calcd for $C_{15}H_{16}Ge$ 270.0464, found 270.0470. Anal. Calcd for $C_{15}H_{16}Ge$: C, 67.01, H, 6.00. Found: C, 67.07, H, 6.05.

Methyldiphenylgermanium chloride, from which authentic samples of **4a** and **4c** were prepared, was synthesized as follows. Methyldiphenylgermane[25] (1.75 g, 7.2 mmol) was dissolved in carbon tetrachloride (25 mL) in a 100 mL round-bottom flask, and then chlorine gas was bubbled through the solution until it assumed a slightly yellow tinge. The chlorine gas source was removed, and the solution was irradiated with a sunlamp for 8 min. Removal of the solvent by vacuum distillation afforded a slightly yellow oil, which was identified as methyldiphenylgermanium chloride[26] (1.97 g, 7.1 mmol, 99%) on the basis of the following spectroscopic data: ^{1}H NMR $\delta = 0.99$ (s, 3H), 7.26−7.30 (m, 6H), 7.50−7.55 (m, 4H); ^{13}C NMR $\delta = 1.91$, 128.84, 130.41, 133.72, 137.76; IR (neat) 3070.8 (m), 2914.0 (w), 2861.2 (w), 1958.9 (w), 1883.9 (w), 1818.6 (w), 1484.9 (m), 1433.1 (s), 1334.9 (m), 1245.0 (m), 1094.1 (s), 1066.7 (m), 1026.6 (m), 802.5 (s), 735.0 (s), 696.9 (s); MS (EI) *m/z* (*I*) = 278 (20), 263 (90), 243 (35), 201 (10), 151 (20), 117 (25), 91 (7), 77 (25); exact mass calcd for $C_{13}H_{13}GeCl$ 277.9917, found 277.9914.

Methoxy- and *tert*-butoxymethyldiphenylgermane (**4a,c**) were synthesized by reaction of methyldiphenylgermanium chloride with methanol and *tert*-butanol, respectively, in dry benzene in the presence of triethylamine.[9] For example, methyldiphenylgermanium chloride (0.25 g, 0.9 mmol) and dry methanol (0.1151 g, 3.6 mmol) were placed in benzene (10 mL) and stirred at room temperature. Triethylamine (0.3636 g, 3.6 mmol) was added rapidly to the stirred solution, causing the immediate formation of a white precipitate. The reaction mixture was stirred under reflux for 24 h (72 h for *tert*-butyl alcohol), cooled and filtered, and then concentrated to ca. 1 mL by vacuum distillation. GC analysis of the crude reaction mixture indicated the conversion of the chloro- to alkoxygermane to be quantitative in both cases. The alkoxygermanes were isolated from the crude reaction mixtures by semipreparative gas chromatography.

Methoxymethyldiphenylgermane (**4a**). ^{1}H NMR $\delta = 0.71$ (s, 3H), 3.44 (s, 3H), 7.10−7.35 (m, 6H), 7.42−7.61 (m, 4H); ^{13}C NMR $\delta = -3.67$, 52.76, 128.57, 129.90, 134.35, 137.61; IR (neat) 3069.9 (m), 2955.3 (m), 2925.9 (s), 2816.8(m), 1962.9 (w), 1884.4 (w), 1829.2 (w), 1484.9 (m), 1431.8 (s), 1376.3 (m), 1185.8 (w), 1095.3 (s), 1052.7 (s), 998.6 (m), 847.7 (m), 790.9 (m); MS (EI) *m/z* (*I*) = 274 (6), 259 (100), 229 (60), 167 (20), 151 (50), 89 (20), 77 (10). Anal. Calcd for $C_{14}H_{16}GeO$: C, 61.62, H, 5.91. Found: C, 61.95, H, 5.88.

***tert*-Butoxymethyldiphenylgermane** (**4c**). ^{1}H NMR $\delta = 0.80$ (s, 3H), 1.18 (s, 9H), 7.22−7.25 (m, 6H), 7.47−7.51 (m, 4H); ^{13}C NMR $\delta = 0.55$, 33.03, 73.17, 128.40, 129.55, 134.26, 140.40; IR (neat) 3071.5 (m), 2973.5 (s), 2886.3 (w), 2857.5 (w), 1950.3 (w), 1882.6 (w), 1817.3 (w), 1431.9 (s), 1361.5 (s), 1240.3 (m), 1192.4 (s), 1095.1 (s), 970.8 (s), 851.7 (w), 613.0 (m); MS (EI) *m/z* (*I*) = 301 (30), 243 (100), 223 (10), 183 (7), 151 (25), 125 (3), 91 (15), 77 (15), 43 (40); exact mass calcd for (M − 15) $C_{16}H_{19}GeO$ 297.0678, found 297.0669.

Preparative irradiations of **1** employed a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.) equipped with 8−10 RPR−2537 lamps. For the synthesis of digermetane **3**, a deoxygenated solution of **1** (0.25 g, 0.9 mmol) in hexane (15 mL) was placed in a quartz photolysis tube sealed with a rubber septum, and irradiated for 8 h. The solvent was removed on the rotary evaporator to yield a slightly yellow oil, the NMR spectrum of which indicated that it consisted of **1** and **3** in a 3:2 ratio. The germene dimer was isolated by radial chromatography using hexane as eluant. After elution of starting material (**1**, 0.15 g), the solvent was changed to 10% dichloromethane in hexane. The product was collected as a colorless oil (0.08 g, 0.16 mmol, 91% yield based on recovered **1**) which crystallized upon addition of a small amount of pentane and cooling to −10 °C. A second recrystallization from pentane afforded the compound as colorless needles (mp 120−121 °C) which were identified as 1,1,3,3-tetraphenyl-1,3-digermetane (**3**) on the basis of the following spectroscopic data: ^{1}H NMR $\delta = 1.62$ (s, 4H), 7.31−7.36 (m, 12H), 7.50−7.56 (m, 8H); ^{13}C NMR $\delta = 7.71$, 128.22, 128.96, 133.67,

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(25) Castel, A.; Riviere, P.; Satge, J.; Ko, H. Y. *Organometallics* **1990**, *9*, 205.

(26) Mochida, K.; Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *J. Am. Chem. Soc.* **1987**, *109*, 7942.

139.53; IR (neat), 3070.2 (m), 2955.3 (m), 2926.2 (m), 1952.5 (w), 1879.7 (w), 1814.8 (w), 1484.6 (m), 1431.4 (s), 1373.7 (m), 1354.4 (m), 1091.8 (s), 954.6 (m), 908.9 (s); MS (EI) *m/z* (*I*) = 482 (10), 406 (15), 391 (50), 305 (100), 271 (5), 243 (40), 227 (40), 151 (50); exact mass calcd for $C_{26}H_{24}Ge_2$ 484.0261, found 484.0302. Anal. Calcd for $C_{26}H_{24}Ge_2$: C, 64.84, H, 5.02. Found: C, 64.64, H, 5.06.

Solutions of **1** (0.1 g, 3.66×10^{-4} mol) in hexane (15 mL) containing 1.0 M of MeOH, MeOD, EtOH, or *t*-BuOH were placed in quartz tubes, sealed with a rubber septum, deoxygenated with a stream of dry argon, and then photolyzed for 1 h. Periodic monitoring of the course of the photolyses by GC revealed the formation of a single detectable product in all cases. The solvent was removed on the rotary evaporator to yield colorless oils containing product and small amounts of residual **1**. The products were isolated by semipreparative GC. Those from photolysis with MeOH and *t*-BuOH were identical to the authentic samples of **4a** and **4c** (vide supra). Those from photolysis with MeOD and EtOH were identified as **4a**-*d* and **4b**, respectively, on the basis of the following spectroscopic data.

Methoxy(methyl-*d*)diphenylgermane (**4a**-*d*) ^{1}H NMR $\delta = 0.69$ (t, 2H), 3.44 (s, 3H), 7.27−7.35 (m, 6H), 7.46−7.61 (m, 4H); ^{13}C NMR $\delta = -4.30, -3.92, -3.54$, 52.77, 128.77, 129.90, 134.34, 137.59; IR (neat) 3069.1 (m), 2926.6 (m), 2854.1 (m), 1960.2 (w), 1889.6 (w), 1824.6 (w), 1486.1 (m), 1431.3 (s), 1157.6 (m), 1094.9 (s), 844.7 (s), 734.2 (s); MS (EI) *m/z* (I) = 275 (5), 259 (100), 244 (20), 229 (70), 168 (20), 151 (60), 125 (30), 105 (15), 77 (10).

Ethoxymethyldiphenylgermane (**4b**) ^{1}H NMR $\delta = 0.71$ (s, 3H), 1.12 (t, 3H), 3.62 (q, 2H), 7.24−7.31 (m, 6H), 7.47−7.51 (m, 4H); ^{13}C NMR $\delta = -3.12$, 19.59, 60.74, 128.54, 129.84, 134.77, 138.07; IR (neat) 3069.4 (m), 2966.4 (m), 2872.7 (m), 1960.8 (w), 1885.1 (w), 1824.9 (w), 1484.8 (m), 1431.5 (s), 1383.3 (m), 1241.5 (w), 1095.7 (s), 1061.1 (s), 1026.6 (w), 848.6 (m), 788.9 (m); MS (EI) *m/z* (*I*) = 288 (5), 273 (50), 243 (70), 229 (100), 165 (20), 151 (80), 123 (15), 77(20); exact mass calcd for $C_{15}H_{18}GeO$ 288.0581, found 288.0569. Anal. Calcd for $C_{15}H_{18}GeO$: C, 62.80, H, 6.32. Found: C, 62.50, H, 6.25.

NMR scale photolyses were carried out in quartz NMR tubes, using ~0.1 M solutions of **1** in cyclohexane−d_{12}. For trapping experiments the solutions also contained 1.0 M of MeOH, EtOH, *t*-BuOH, or HOAc. These experiments gave comparable results to those described above; in addition, the formation of ethylene was evident from the appearance of a singlet at 5.30 ppm, which was verified by the addition of a small amount of an authentic sample to one of the photolysis mixtures. Attempted acetone trapping experiments were carried out using a 0.03 M solution of **1** containing 0.07 M dry acetone. Photolysis to ~20% conversion of **1** led only to the formation of a polymer characterized by a singlet at 0.19 ppm and broad resonances in the aromatic region.

NLFP experiments employed the pulses (248 nm; ca. 16 ns; 70−120 mJ) from a Lumonics 510 excimer laser filled with F_2/Kr/He mixtures, and a microcomputer-controlled detection system.[27] The system incorporates a brass sample holder, the temperature of which is controlled to within 0.1 °C by a VWR 1166 constant temperature circulating bath. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (4.4×10^{-3} M), and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple which was inserted directly into the flow cell. Quenchers were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (6−15 points, depending on whether the plots were linear or curved) which spanned at least 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

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(27) Leigh, W. J.; Workentin, M. S.; Andrew, D. *J. Photochem. Photobiol. A*: **1991**, *57*, 97.