the proton at C5 and a small coupling to the proton at C6.

In a control experiment we also measured the CIDNP of deoxygenated solutions of DMUM (100 mM) and 2MInd (25 mM) in acetonitrile. The spectra are shown in Figure 2. DMUM shows emission at 3.26 and 3.34 ppm due to the two methyl groups at N3 and N1, respectively, and enhanced absorptions at 7.37 ppm for the proton at C6. 2MInd shows again enhanced absorption at 2.46 ppm and, in addition, emission at 6.19 ppm for the proton at C3, as well as weak emission and absorption for the aromatic protons. The phases can be explained again with the aid of Kaptein's rules by assuming conditions similar to those in the DMUD case for geminate recombination, but now with a large and negative coupling to the C6 and little coupling to the C5 proton (7.37 vs 5.66 ppm). This agrees with spin density calculations for DMUM radical anion which predict high spin density at C6 and small spin density at C5.[13]

There is a distinct difference between the CIDNP spectra of DMUM formed from DMUD cleavage (Figure 1) or from the purely cyclic ET process (Figure 2). This is the consequence of the difference of precursors, i.e., the parent radical anions and their spin density distributions. We did not observe any CIDNP signal due to the C6 ring proton for DMUM after DMUD cleavage which could arise from geminate[16] and from nongeminate $2MInd^+$ $DMUM^-$ pairs. This implies that the splitting of $DMUD^-$ does not compete effectively with the geminate reverse ET and that the concentration of free $DMUM^-$ is low. Further work is in progress to elucidate more kinetic information and donor and solvent dependences.

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Investigation of the Gas-Phase Reaction of Trimethylsilyl Radicals with HBr: Measurement of the $(CH_3)_3Si-H$ Bond Strength

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There is considerable variation between estimates of the Si–H bond dissociation enthalpy in trimethylsilane, $D_{298}((CH_3)_3Si-H)$. Walsh suggested a value equal to $D_{298}(SiH_3-H)$ mainly on the basis of iodination kinetics,[1] while McKean et al.[2] and Bernheim et al.[3] suggested that the three methyl groups weaken the Si–H bond by 24 and 57 kJ mol^{-1}, respectively, on the basis of vibrational spectroscopy. By contrast, Ding and Marshall proposed a bond strengthening of 14 kJ mol^{-1} on the basis of bromination experiments.[4] In that work the temperature dependence of the measured reverse rate constant k_{-1} for

$$(CH_3)_3Si + HBr \rightleftharpoons (CH_3)_3SiH + Br \qquad (1)$$

was combined with an *estimated* activation energy for k_1 in a second-law analysis. We have now carried out the first measurement of k_1 at room temperature to obtain the equilibrium constant $K_{eq} = k_1/k_{-1}$, and hence the thermochemistry, via a third-law method, without kinetic assumptions. The spread of ΔH implied by the range of $D_{298}((CH_3)_3Si-H)$ corresponds to a factor of 10^{12} variation in K_{eq}, so that even an approximate determination of k_1 dramatically reduces the uncertainty in the thermochemistry. We find $k_1 \approx 8 \times 10^{-11}$ cm^3 s^{-1}, which implies an Si–H bond strength of 398 ± 2 kJ mol^{-1}, about 14 kJ mol^{-1} greater than that in SiH_4.[5]

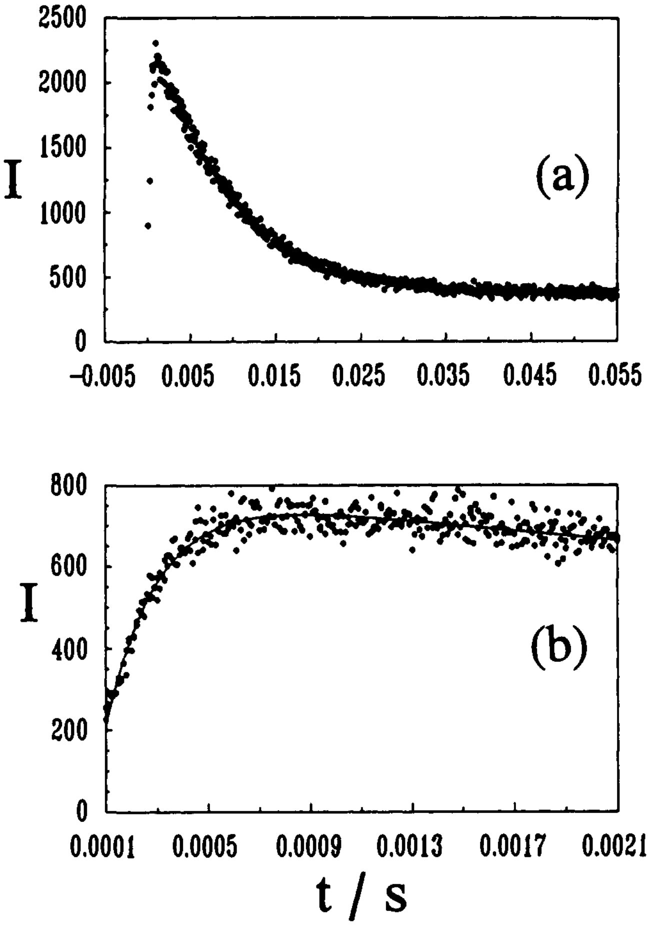

Figure 1. Plot of fluorescence intensity *I* (including background scattered light) vs time *t* obtained at (a) low and (b) high time resolutions, corresponding to the conditions of Figure 2.

The flash photolysis apparatus has been described in detail elsewhere.[6,7] Reagents were purified by distillation and stored in the dark. Trimethylsilyl radicals were generated by pulsed photolysis of trimethylsilyl iodide (Hüls America, Inc.) with a small flash lamp through Suprasil quartz optics, and preliminary experiments[8] with resonance fluorescence detection confirmed that I atoms were formed. Halogen exchange between $(CH_3)_3SiI$ and HBr is negligible.[9] $(CH_3)_3Si$ reacted with excess HBr (Matheson Gas Products) diluted in Ar bath gas under pseudo-first-order conditions. The course of reaction was followed by monitoring the product Br by means of time-resolved atomic resonance fluorescence with pulse counting and multichannel scaling. A few millibars of H_2 was added to equilibrate $Br(^2P_{1/2})$ and $Br(^2P_{3/2})$,[10] so that effectively only $Br(^2P_{3/2})$ was detected. k_1 was found to be almost gas-kinetic; thus reaction 1 cannot be significantly endothermic. This rules out $Br(^2P_{1/2})$, excited by 44.0 kJ mol^{-1},[11]

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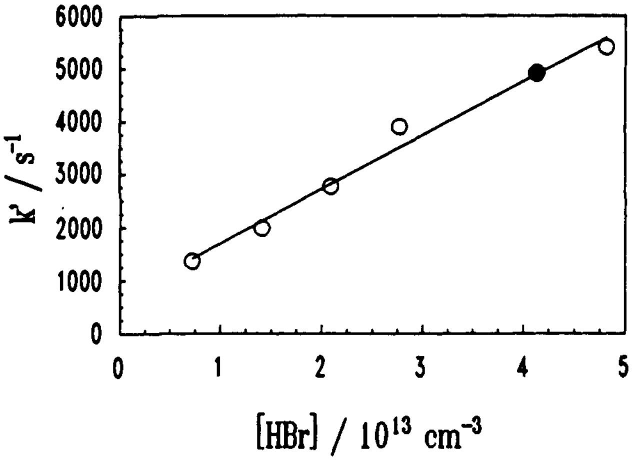

Figure 2. Plot of pseudo-first-order rate constants for formation of Br vs [HBr] at 291 K and 47 mbar. The filled circle corresponds to the data of Figure 1.

Table I. Summary of Kinetic Measurements on $(CH_3)_3Si + HBr$[a]

P, mbar	τ_{res}, s	F, J	$[(CH_3)_3SiI]$, 10^{14} cm^{-3}	k_1, 10^{-11} cm^3 s^{-1}
45.2	0.7	4.05	3.06	8.5 ± 0.6
47.3	0.8	5.00	3.16	10.5 ± 0.7
47.3	0.8	2.45	3.16	10.1 ± 0.6
46.0	1.0	4.05	4.69	5.8 ± 0.2
46.1	0.6	4.05	3.03	5.7 ± 0.4
45.5	0.5	4.05	1.21	10.2 ± 0.2
32.0	0.5	4.05	2.46	5.2 ± 0.7
31.2	0.5	4.05	2.44	6.0 ± 0.6

[a] Made between 289 and 296 K, with a maximum [HBr] of typically 5×10^{13} cm^{-3}. 1σ statistical precision quoted for k_1.

as a major product. The time dependence of [Br] was interpreted according to the following scheme in addition to reaction 1:

$$(CH_3)_3Si \rightarrow \text{pseudo-first-order loss by processes which do not generate Br} \quad (2)$$

$$Br \rightarrow \text{pseudo-first-order loss by diffusion and other slow processes} \quad (3)$$

Other radicals which might be created photolytically and could lead to Br production are H and CH_3, but their reactions with HBr are more than 1 order of magnitude slower than that of $(CH_3)_3Si$.[10,12–14] An alternative product channel for reaction 1, formation of a bromide and atomic H, was found to be negligible in tests using Lyman-α fluorescence detection.[8] As shown in similar experiments involving the reactions of H, alkyl, and thiyl radicals with HBr,[10,12,13,15,16] [Br] is expected to vary as

$$[Br] = A \exp(-k_3 t) - B \exp(-k' t) \quad (4)$$

where $k' = k_1[HBr] + k_2$. We obtained the four parameters of eq 4 from nonlinear least-squares fits to fluorescence decays such as that shown in Figure 1 (the first ≈100 μs are obscured by scattered light from the photolysis flash) and derived k_1 as the slope of a linear plot of k' vs [HBr] as shown in Figure 2. k_3 describes the loss of Br by, e.g., diffusion and a slow reaction with $(CH_3)_3SiI$.[8] k_2 was large, in the range of 500–3000 s^{-1}, and so cannot reflect diffusion alone. Wine and co-workers observed similar rapid alkyl radical disappearance and speculated about roles for impurities such as O_2 or traces of Br_2 or I_2 in their reactor;[10] similar arguments can be applied here. It is also possible that $(CH_3)_3Si$ reacts readily with $(CH_3)_3SiI$.

The k_1 results are summarized in Table I and show no consistent variation with experimental parameters such as pressure P, average gas residence time τ_{res}, flash energy F, and precursor concentration. The mean k_1 is $(7.8 \pm 0.8) \times 10^{-11}$ cm^3 s^{-1} (1σ precision), about twice the rate constant for $t\text{-}C_4H_9 + HBr$ of 3×10^{-11} cm^3 s^{-1} at 298 K.[10,14,15] k_{-1} at this temperature is $(8.0 \pm 1.6) \times 10^{-15}$ cm^3 s^{-1} under conditions where the low-lying states of Br were equilibrated, i.e., the Br was essentially all present as $^2P_{3/2}$.[4] Thus we may obtain $K_{eq} = k_1/k_{-1} = 9.75 \times 10^3$. Bearing in mind that detection of product appearance rather than reactant consumption is often more vulnerable to secondary chemistry, we conservatively allow for a factor of 2 inaccuracy in K_{eq}. This yields $\Delta G = -22.8 \pm 1.7$ kJ mol^{-1}. The value of $\Delta S_{298} = -28.6 \pm 2$ J K^{-1} mol^{-1} for reaction 1 is derived from the accurately known entropies of HBr and Br,[17] coupled with the difference in S between $(CH_3)_3Si$ and $(CH_3)_3SiH$ calculated from ab initio data.[4] The uncertain contributions of internal rotors within the silicon species thus largely cancel. This yields $\Delta H_{298} = -31.3$ kJ mol^{-1} $= D_{298}(\text{H–Br})^{17} - D_{298}((CH_3)_3\text{Si–H})$, and hence the bond dissociation enthalpy is 398 ± 2 kJ mol^{-1}. The confidence interval allows for errors in K_{eq} and ΔS. This value confirms the previous estimate and the implications for other bond strengths and enthalpies of formation given earlier[4] but eliminates the need for kinetic assumptions and reduces the uncertainty. Methyl substitution significantly increases the Si–H bond strength in silane, and the best estimate of $\Delta H_{f,298}((CH_3)_3Si)$ is 17 ± 4 kJ mol^{-1}, where the main source of uncertainty is now $\Delta H_{f,298}((CH_3)_3SiH)$.[18] These results imply a negative activation energy of about -3 kJ mol^{-1} for k_1, which will be investigated in future work.

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Selective Free-Radical Halogenation of Polyphenylsilane

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Polysilanes constitute a novel class of materials with unique electronic properties.[1] The unusual properties of these polymers are influenced by the polymer conformation, the molecular weight, and the substituents attached to the polymer backbone.[2] Conventional methods of synthesizing these materials are intolerant of many functional groups and offer limited potential for control of stereochemistry or molecular weight.[3,4] In contrast, recently

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