Articles

Kinetic and Product Studies of the Reaction of Triorganosilanes with Dimethyldioxirane

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The oxidation of a variety of triorganosilanes by dimethyldioxirane afforded the corresponding silanols in quantitative yield. The reactions are performed at room temperature using acetone or CCl_4 as the solvent. Under similar conditions, $(Me_3Si)_3SiH$ gave silanol in 80−90% yield together with other identified products. Rate constants for these reactions were measured by following the disappearance of the dimethyldioxirane absorption at 335 nm. Depending on the substituents at the SiH moiety, the reactivities cover ca. 4 orders of magnitude (from 5.8×10^{-3} M^{-1} s^{-1} for $(Me_3SiO)_3SiH$ at 25 °C to 14.5 M^{-1} s^{-1} for $(Me_3Si)_3SiH$ at 15 °C). Arrhenius parameters were determined for a few representative substrates. The reaction mechanism in terms of a concerted oxygen insertion vs radical path is discussed in some detail.

Introduction

Silanols are of considerable importance in both organic synthesis[1] and industrial applications.[2] The main approach for silanol synthesis is the direct oxidation of the Si−H moiety, and both stoichiometric oxidants[3,4] and catalytic methods[5] have been reported. However, the majority of the existing methods for the preparation of silanols give the corresponding siloxane as an undesired side product. The use of dioxiranes in a stoichiometric fashion for the oxidation of silicon hydrides is limited, although the method appears to be an efficient process. Adam et al. reported the oxidation of Et_3SiH, $PhMe_2SiH$, and α-NpPhMeSiH with methyl(trifluoromethyl)dioxirane at −20 °C and of α-NpPhMeSiH with dimethyldioxirane at 0 °C in CH_2Cl_2 as the solvent.[3] Rate constants (at 0 °C) of 0.78 and 450 M^{-1} s^{-1} for the oxidation of α-NpPhMeSiH with dimethyldioxirane and methyl(trifluoromethyl)dioxirane, respectively, were also measured.[3]

A solution of dimethyldioxirane (DMD) in acetone is a well-established oxidant for a variety of organic compounds such as alkanes, ethers, and alcohols.[6] The reaction mechanism for these processes has attracted considerable interest and is still under dispute. Of interest to us is the transformation of a C−H bond into the corresponding C−OH bond, for which Adam et al.[7] reported evidence for a concerted pathway through a spiro transition state and Minisci et al.[8] described experiments that are in favor of a radical path. Data on the oxidation of a hypersensitive radical probe[9] and on the regioselectivity of intramolecular oxidation[10] suggest that the concerted pathway is the main route. High-level ab initio studies support a highly polar asynchronous transition state with considerable diradical character which is common for both concerted oxygen

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(1) (a) For example, see: *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1−3. (b) For recent reports on the synthetic transformation of silanols, see: Uehara, S.; Takaku, K. Shinokubo, H.; Oshima, K. *Synlett* **1998**, 1096−1098. Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893−7896. Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Org. Lett.* **1999**, *1*, 299−301. Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565−568. Denmark, S. E.; Sweis, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 6439−6440.

(2) For a review, see: Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147−262.

(3) Adam, W.; Mello, R.; Curci, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 890−891.

(4) Cavicchioli, M.; Montanari, V.; Resnati, G. *Tetrahedron Lett.* **1994**, *35*, 6329−6330.

(5) For recent examples, see: Schubert, U.; Lorenz, C. *Inorg. Chem.* **1997**, *36*, 1258−1259. Adam, W.; Mitchell, C. M.; Saha-Möller, C. R.; Weichold, O. *J. Am. Chem. Soc.* **1999**, *121*, 2097−2103. Coupar, P. I.; Jaffrès, P.-A.; Morris, R. E. *J. Chem. Soc., Dalton Trans.* **1999**, 2183. Adam, W.; Saha-Möller, C. R.; Weichold, O. *J. Org. Chem.* **2000**, *65*, 2897−2899. Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011−12012.

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(7) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparrini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Angela Velosa, L.; Weikötz, S.; Winde, R. *Chem. Eur. J.* **1997**, *3*, 105−109.

(8) Bravo, A.; Fontana, F.; Fronza, G.; Minisci, F.; Zhao, L. *J. Org. Chem.* **1998**, *63*, 254−263.

(9) Simakov, P. A.; Choi, S.-Y.; Newcomb, M. *Tetrahedron Lett.* **1998**, *39*, 8187−8190.

(10) Yang, D.; Wong, M.-K.; Wang, X.-C.; Tang, Y.-C. *J. Am. Chem. Soc.* **1998**, *120*, 6611−6612.

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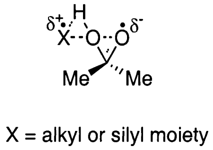
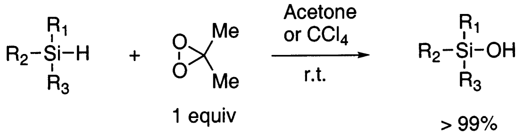


Figure 1. Representation of the asynchronous transition state.

Scheme 1[a]



[a] Starting silane (reaction time): Et_3SiH (<5 min); *t*-$BuMe_2SiH$ (<5 min); $PhMe_2SiH$ (<5 min); Ph_3SiH (10 min); $PhMeSi(H)SiMe_3$ (<1 min); $(Me_3SiO)Me_2SiH$ (15 min); $(Me_3SiO)_2MeSiH$ (30 min); $(Me_3SiO)_3SiH$ (3 h).

insertion into the CH bond and the formation of a radical pair (Figure 1, X = alkyl group).[11,12] Theoretical results reconcile the apparently contradictory experimental data and suggest that the proportion of products from electrophilic attack compared to radical-derived products will depend primarily on the reaction thermochemistry.[11] Theory predicted that the energy of the C–H bond should be less than 83.5 kcal mol^{-1} in order for the radical path with DMD to be exothermic.[11c] Recently, DMD-induced homolysis of the C–C bond in strained alkanes has also been reported.[13]

Herein we report detailed product and kinetic studies of the reaction of DMD with a variety of triorganosilanes, where the Si–H bond strength varies from 84.0 to ca. 100 kcal mol^{-1}.[14]

Results and Discussion

Product Studies. To a solution of ca. 0.1 M DMD in acetone kept under argon at 25 °C was added an equimolar amount of silane, and the course of the reaction was followed qualitatively by gas chromatography. The silane was converted into the corresponding silanol. After completion of the reaction and removal of the solvent, the silanol was obtained in quantitative yield and high purity (Scheme 1). In oxygenated solutions or by replacing acetone with CCl_4, the same results have been obtained. Only in the case of Ph_3SiH has silyl chloride also been detected in less than 1% yield by GC analysis. Moreover, 2 equiv of DMD was necessary for the complete oxidation of 1,1,2,2-tetraisopropyldisiloxane (Scheme 2). When 1 equiv of DMD was used, the silanol and silandiol were formed in a 1:2 ratio.

Scheme 2

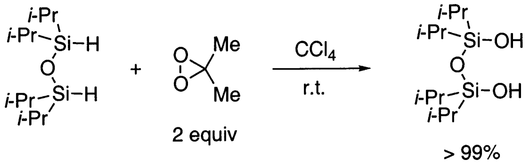
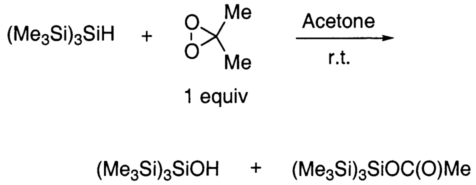


Table 1. Reaction of $(Me_3Si)_3SiH$ with Dimethyldioxirane

entry	conditions[a]	time, min	product	yield,[b] %
1	acetone, 20 °C	<1	$(Me_3Si)_3SiOH$	79
			$(Me_3Si)_3SiOC(O)Me$	16
2	acetone, O_2, 20 °C	<1	$(Me_3Si)_3SiOH$	>99
3	acetone, −70 °C	10	$(Me_3Si)_3SiOH$	>99
4	acetone, −70 °C, *hν*	10	$(Me_3Si)_3SiOH$[c]	88
			$(Me_3Si)_3SiOC(O)Me$	5
5	CCl_4, 20 °C[d]	<1	$(Me_3Si)_3SiOC(O)CF_3$	90
			$(Me_3Si)_3SiCl$	10

[a] Deoxygenated solutions except for entry 2. [b] Conversions higher than 80%. Yields are based on the converted silane. [c] Small amounts of $(Me_3Si)_3SiSi(SiMe_3)_3$ were also formed as a byproduct. [d] In the presence of 1 equiv of $CF_3C(O)OC(O)CF_3$ (see text).

Scheme 3



The reaction of DMD with $(Me_3Si)_3SiH$ behaved somewhat differently. The reaction under normal conditions (Table 1, entry 1) afforded the expected silanol in 79% yield together with the corresponding silyl acetate in 16% yield (Scheme 3).[15] A 10-fold excess of $(Me_3Si)_3SiH$ did not influence the product distribution. When the reaction was run in the presence of 0.1 M $CF_3C(O)OC(O)CF_3$, the $(Me_3Si)_3SiOH$ was quantitatively transformed into $(Me_3Si)_3SiOC(O)CF_3$. On the other hand, the formation of $(Me_3Si)_3SiOH$ was quantitative when the reaction was run under oxygen (entry 2) or at −70 °C (entry 3). However, in this last reaction, when repeated in the presence of visible light (entry 4), the silyl acetate was again formed in an appreciable amount together with small amounts of $(Me_3Si)_3Si–Si(SiMe_3)_3$. When CCl_4 was used as the solvent at 20 °C, the $(Me_3Si)_3SiOC(O)CH_3$ was replaced by $(Me_3Si)_3SiCl$, although a quantitative analysis was difficult, due to the almost identical retention times of silyl alcohol and silyl chloride in GC analysis. In this respect, the quantification was performed by running the reaction in the presence of $CF_3C(O)OC(O)CF_3$, since the alcohol is transformed into $(Me_3Si)_3SiOC(O)CF_3$ (entry 5).

The oxidation of α-NpPhMeSiH by dioxiranes was reported to occur with a complete retention of configuration, and consequently, an insertion mechanism was suggested (cf. Figure 1, X = silyl group).[3] Another possibility is the molecule-induced homolysis to give two

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(11) (a) Du, X.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 6480–6483. (b) Shustov, G. V.; Rauk, A. *J. Org. Chem.* **1998**, *63*, 5413–5422. (c) Glukhovtsev, M. N.; Canepa, C.; Bach, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 10528–10533. (d) Freccero, M.; Gandolfi, R.; Sarzi-Amadè, M.; Rastelli, A. *Tetrahedron Lett.* **2001**, *42*, 2739–2742.

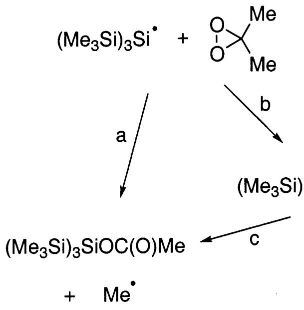
(12) The bifurcation point is located about 2 kcal mol^{-1} below and *after* the transition structure.[11b]

(13) Fokin, A. A.; Tkachenko, B. A.; Korshunov, O. I.; Gunchenko, P. A.; Schreiner, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 11248–11252.

(14) The competition between concerted and radical pathways for the DMD decomposition in acetone has been the subject of recent product and kinetic studies, which show that the radical path accounts for 20–25% at 56 °C. See: Grabovskii, S. A.; Suvorkina, E. S.; Kabal'nova, N. N.; Khursan, S. L.; Shereshovets, V. V. *Russ. Chem. Bull. (Engl. Transl.)* **2000**, *49*, 1332–1337. Khursan, S. L.; Grabovskii, S. A.; Kabal'nova, N. N.; Galkin, E. G.; Shereshovets, V. V. *Russ. Chem. Bull. (Engl. Transl.)* **2000**, *49*, 1338–1348.

(15) $(Me_3Si)_3SiOH$ was previously prepared by hydrolysis of the corresponding halides; see: Boo, B. H.; Kang, H. K.; Kang, S. K.; Lee, S. S.; Kim, D.; Lee, M. H. *J. Organomet. Chem.* **1992**, *436*, 1–9. Kornev, A. N.; Chesnokova, T. A.; Semenov, V. V.; Kurskii, Y. A. *Russ. Chem. Bull. (Engl. Transl.)* **1995**, *44*, 1107–1110.

Scheme 4



radicals in the cage, which combine to give the observed products after decomposition.[8] By this model, diffusible silyl radicals can be obtained when the cage radicals are escaping. The fact that our experiments carried out in CCl_4 afforded the corresponding silanols in quantitative yields excludes the involvement of diffusing silyl radicals as intermediates. Indeed, $Et_3Si^•$ and *t*-$BuPh_2Si^•$ radicals abstract a chlorine atom from CCl_4 with rate constants of $>10^9$ M^{-1} s^{-1} at room temperature.[16]

On the other hand, silyl radicals seem to be important intermediates in the case of $(Me_3Si)_3SiH$.[17] We suggest that, besides the direct formation of silanol, a parallel radical chain mechanism is also operative.[18] That is, $(Me_3Si)_3Si^•$ radicals, initially generated by a "spontaneous" reaction between $(Me_3Si)_3SiH$ and DMD, attack the peroxyl moiety of the dioxirane in a synchronous (step a) or stepwise (steps b and c) S_H2-type process to give silyl acetate and methyl radical (Scheme 4). The reaction of $Me^•$ radical with $(Me_3Si)_3SiH$ completes the chain cycle.[19] The fact that a 10-fold excess of $(Me_3Si)_3SiH$ (i.e. 1 M) did not influence the product distribution favors the synchronous mode for the following reasons: (i) the rate constant of $Me_3CO^•$ radical with $(Me_3Si)_3SiH$ is known to be 1.1×10^8 M^{-1} s^{-1} at 24 °C[20] and a similar value is expected by replacing $Me_3CO^•$ with alkoxyl radical **1**, and (ii) the rate constant for β-scission of radical **1** (path c) is assumed to be similar to the β-scission of cumyloxyl radical, which is between 2×10^5 and 2×10^6 s^{-1} at 25 °C, depending on the solvent polarity.[21] In oxygenated solution, diffusible $(Me_3Si)_3Si^•$ radicals are efficiently scavenged by O_2 and their participation in the chain reaction is thereby prevented.

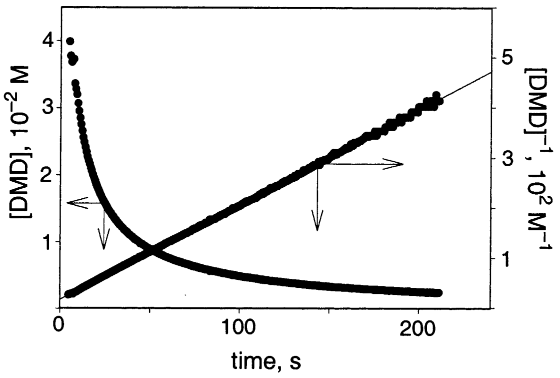


Figure 2. Decay of DMD observed at 335 nm in the presence of 0.05 M $PhMe_2SiH$ at 37 °C and second-order kinetic fits to the data.

Table 2. Absolute Rate Constants and Arrhenius Parameters for the Reaction of Dimethyldioxirane with a Variety of Silanes[a]

hydrosilane	*T*, °C	*k*, M^{-1} s^{-1}	log(*A*/ M^{-1} s^{-1})	E_a, kcal mol^{-1}
Et_3SiH	30	1.82 ± 0.07	7.16 ± 0.20	9.52 ± 0.24
t-$BuMe_2SiH$	30	1.67 ± 0.22	7.30 ± 0.14	9.86 ± 0.19
$PhMe_2SiH$	37	1.75 ± 0.13		
Ph_3SiH	27	0.71 ± 0.11		
$(Me_3SiO)Me_2SiH$	26	1.22 ± 0.06	8.20 ± 0.30	11.07 ± 0.34
$(Me_3SiO)_2MeSiH$	25	0.219 ± 0.013	8.17 ± 0.12	12.08 ± 0.18
$(Me_3SiO)_3SiH$	25	0.0059 ± 0.0005	7.19 ± 0.06	12.88 ± 0.18
$(Me_3Si)MePhSiH$	25	13.0 ± 1.7		
$(Me_3Si)_3SiH$	15	14.5 ± 0.8[b]		

[a] Errors correspond to one standard deviation. [b] Derived from competitive studies (see text).

When acetone is replaced with CCl_4, the aforementioned radical chain reaction is substituted by the radical chain dechlorination of the solvent. The silyl acetate was not detected by the reaction mixture, which suggests $[(Me_3Si)_3SiCl]/[(Me_3Si)_3SiOC(O)Me] \geq 100$ on the basis of the sensibility of the GC analysis. Since the rate constant of $(Me_3Si)_3Si^•$ radical with CCl_4 is 1.7×10^8 M^{-1} s^{-1} at 20 °C[22] and $[CCl_4] \approx 100[DMD]$, an upper limit of 10^8 M^{-1} s^{-1} can be calculated for the attack of $(Me_3Si)_3Si^•$ radical at dioxirane (S_H2 reaction).

Kinetic Studies. The reactions of DMD with a variety of silanes were followed spectrophotometrically at 335 nm, where DMD exhibits a weak optical absorption ($\lambda_{max} = 335$ nm and $\epsilon_{max} = 14$ M^{-1} cm^{-1}).[23] The initial concentrations of DMD and silane were the same and in the range of 0.04–0.1 M. Figure 2 shows the disappearance of DMD in the presence of $PhMe_2SiH$ and the second-order kinetic fits to the data as an example. The absolute rate constants for a variety of silicon hydrides obtained by this approach are reported in Table 2. Each value is the average of at least three independent measurements. The Arrhenius parameters were obtained for some of these hydrosilanes and are also listed in Table 2, while the corresponding plots are shown in Figure 3. The activation parameters were obtained in a relatively small temperature interval (ca. 40 °C; cf. Figure 3), and therefore, the errors given in Table 2 should be read with caution.

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(16) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229–1251.

(17) For the radical chemistry of $(Me_3Si)_3SiH$, see: Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188–194. Chatgilialoglu, C.; Ferreri, C.; Gimisis, T. In *The Chemistry of Organic Silicon Compounds*; Rappoport, S., Apeloig, Y., Eds.; Wiley: London, 1998; Vol. 2, pp 1539–1579.

(18) A reviewer suggested that the formation of silyl acetate could be the result of a less effective cage coupling of the radical pair due to the steric effect of $(Me_3Si)_3Si^•$ radicals.

(19) The rate constant for the reaction of methyl radical with $(Me_3Si)_3SiH$ is unknown. However, primary alkyl radical abstracts hydrogen from $(Me_3Si)_3SiH$ with $k = 3.8 \times 10^5$ M^{-1} s^{-1} at 27 °C. Since Bu_3SnH and $(Me_3Si)_3SiH$ are parallel in reactivity toward alkyl radical, and methyl radical reacts with Bu_3SnH ca. 5 times faster than primary alkyl radicals at room temperature, we estimate $k \approx 2 \times 10^6$ M^{-1} s^{-1} for the reaction of methyl radical with $(Me_3Si)_3SiH$.[20] On the other hand, Minisci and co-workers in their study suggested that methyl radical reacts with DMD to give $CH_3C(O)OCH_3$ with $k \approx 10^6$ M^{-1} s^{-1}.[8] The absence of $CH_3C(O)OCH_3$ in our reaction mixture suggests that the difference between the two estimated values should be larger.

(20) Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67–112.

(21) For solvent effects at 30 °C, see: Avida, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466–470. For activation parameters in Frigen 113, see: Zytowski, T.; Fischer, H. *J. Am. Chem. Soc.* **1997**, *119*, 12869–12878.

(22) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 2492–2494.

(23) Adam, W.; Hadjiarapoglou, L. *Top. Curr. Chem.* **1993**, *164*, 45–62.

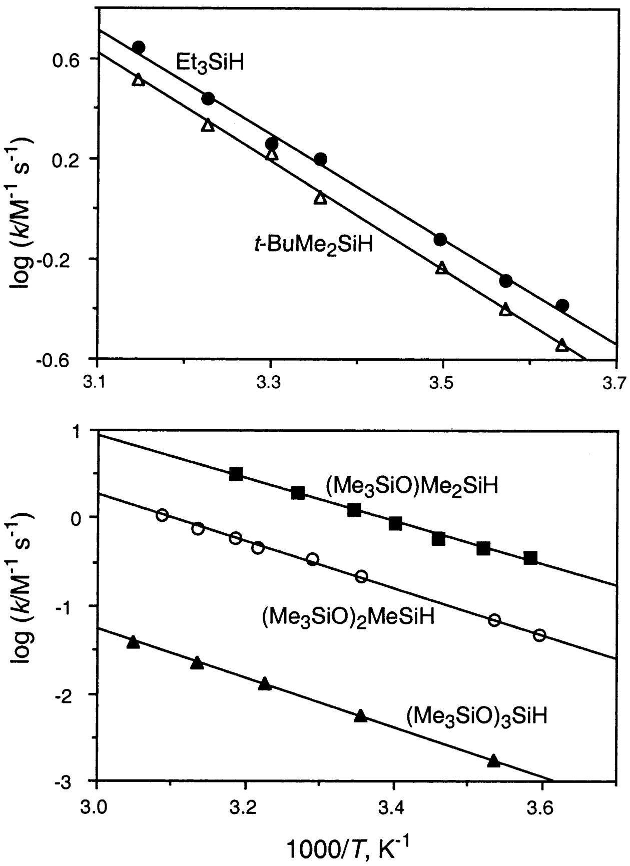


Figure 3. Arrhenius plots for the reaction of DMD with silicon hydrides in acetone solutions.

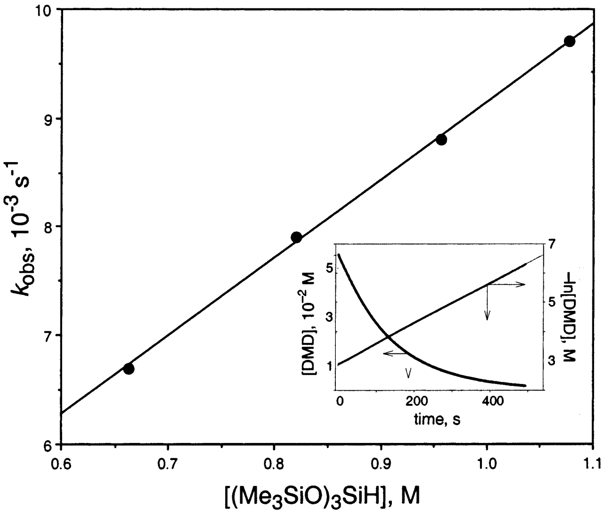
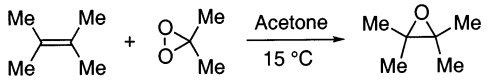


Figure 4. Plot of the observed rate constant k_{obs} for the reaction of DMD and $(Me_3SiO)_3SiH$ at 25 °C. Inset: Representative trace monitored at 335 nm and the corresponding semilogarithmic plot ($[(Me_3SiO)_3SiH] = 0.82$ M).

For comparison, the reaction of DMD with $(Me_3SiO)_3SiH$ was also studied under pseudo-first-order conditions. The time profile of the disappearance of DMD (Figure 4, inset) leads to a pseudo-first-order rate constant, k_{obs}, and was measured at a number of different $(Me_3SiO)_3SiH$ concentrations. From the slope of the linear plot (Figure 4), the bimolecular rate constant was found to be $(7.2 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, which is in reasonable agreement with the value of $(5.9 \pm 0.5) \times 10^{-3}$ M^{-1} s^{-1} obtained under second-order conditions if the change in the medium is considered (up to 40% silane under pseudo-first-order conditions).

Scheme 5



The reaction of DMD with $(Me_3Si)_3SiH$ was found to be faster than those described above, and therefore, the rate constant could not be measured with accuracy. However, kinetic information of this reaction could be obtained from the competition with the epoxidation of 2,3-dimethyl-2-butene (Scheme 5). Indeed, at 15 °C three independent experiments gave $k/k_{epox} = 2.94 \pm 0.09$, where k and k_{epox} are the rate constants for the reactions of silane and olefin, respectively. The disappearance of DMD in the presence of 2,3-dimethyl-2-butene was followed at 15 °C under second-order conditions, and $k_{epox} = 4.93 \pm 0.68$ M^{-1} s^{-1} was obtained as an average of three measurements, which is in agreement with the previously reported $k_{epox} = 7.1$ M^{-1} s^{-1} at 25 °C.[24] From the k_{epox} and k/k_{epox} data, one obtains $k = 14.5 \pm 0.8$ M^{-1} s^{-1} at 15 °C for the reaction of DMD with $(Me_3Si)_3SiH$.

The previous data available from Adam et al. for α-NpPhMeSiH with DMD ($k = 0.78$ M^{-1} s^{-1} at 0 °C)[3] are of the same order of magnitude as our values, although they are not directly comparable. The rate constants increase along the series $(Me_3SiO)_3SiH$ < $(Me_3SiO)_2MeSiH$ < $(Me_3SiO)Me_2SiH$ < $(alkyl)_3SiH$ < $(Me_3Si)PhMeSiH$ < $(Me_3Si)_3SiH$. The Si−H bond dissociation enthalpies of these compounds decrease along the series from ca. 100 kcal mol^{-1} for the fully silyloxy substituted silane to 84.0 kcal mol^{-1} for $(Me_3Si)_3SiH$.[25] Hence, the reaction is favored by an increasing exothermicity. However, the trends can also be interpreted in terms of polar effects, as suggested by the polar asynchronous transition state of Figure 1.[11] Indeed, the positive charge at the silyl moiety is stabilized by electron-donating substituents such as Me_3Si. On the other hand, electron-withdrawing substituents such as Me_3SiO would disfavor the charge separation, since the dioxirane molecule is also electrophilic. Therefore, the observed reactivity order can be attributed to both enthalpic and polar effects that operate in the same direction. The k values for phenyl-substituted silanes, i.e., $PhMe_2SiH$ and Ph_3SiH, seem to be anomalously low with respect to their Si−H bond dissociation enthalpies. However, this also points to parallel enthalpic and polar effects, because the polar contribution is reduced in reactions involving the phenyl substituents.[26] The aver-

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[24] Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* **1987**, *28*, 3311−3314. Murray, R. W.; Gu, D. Q. *J. Chem. Soc., Perkin Trans. 2* **1994**, 451−453.

[25] The Si−H bond strength of some of these silanes is well-known: i.e., 84.0, 90.3, and 95.1 for $(Me_3Si)_3SiH$, $Me_3SiSi(H)Me_2$, and Et_3SiH, respectively.[20] The remaining compounds can be only evaluated qualitatively. Indeed, the influence of the substituent on Si−H bond strength has been empirically discussed; see: Chatgilialoglu, C. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, The Netherlands, 1988; pp 115−123.

[26] (a) If the transferred charges are delocalized over the reactants, the polar effect should be smaller; see: Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340−1371. (b) In triphenylsilylium ion there is considerable conjugation of the phenyl rings with empty orbital on silicon; see: Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, H. W.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001−5008.

age frequency factor from Table 2, i.e., $\log(A/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 7.6$, corresponds to an activation enthropy[27] of $\Delta S^{\ddagger}{}_{298} = -25.8$ cal mol^{-1} K^{-1}. This is in reasonable agreement with the theoretical value of $\Delta S^{\ddagger}{}_{298} = -20.1$ cal mol^{-1} K^{-1} calculated for the oxidation of Me_3CH by dioxirane via the transition state of Figure 1.[11b]

Conclusion

Our results show that DMD transforms triorganosilanes into the corresponding silanols in excellent yields. Both product and kinetic studies agree with a dominant concerted pathway through a transition state with considerable charge-transfer and diradical character (cf. Figure 1). Substituents that stabilize the development of a silylium ion character (i.e., Me_3Si) are also those that produce a weakening of the Si−H bond and reduce the activation barrier. Theory predicted that the energy of the X−H bond should be less than 83.5 kcal mol^{-1} in its reaction with DMD for the radical reaction to be exothermic.[12] Indeed, the case of $(Me_3Si)_3SiH$ shows the occurrence of a second pathway, which unequivocally involves freely diffusing silyl radicals.

Experimental Section

Product Studies. Dimethyldioxirane (DMD) was prepared by following the known procedure.[28] Starting silanes were commercially available from Aldrich or Fluka and used without further purification. A solution of DMD under argon was kept at the desired temperature for 5 min prior to silane addition. The reactions were monitored by GC. After reaction completion, the solvent was removed and the corresponding silanol was obtained as a pure material. All products have been fully characterized (see the Supporting Information).

Kinetic Measurements. The disappearance of DMD in the presence of a silane was followed spectrophotometrically at 335 nm, where it absorbs with an extinction coefficient of 14 M^{-1} cm^{-1}.[23] A Perkin-Elmer Lambda 20 UV/vis spectrometer with a thermostated block, Perkin-Elmer PTP-6 Peltier System, was used. The starting concentrations of DMD and silane were the same and were in the range of 0.04−0.1 M. The experiments were carried out under argon in a thermostated cell reactor having a 1 cm optical path. The solution of DMD was kept at the desired temperature for 5 min prior to the silane addition. Detailed kinetic data are reported in the Supporting Information.

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Supporting Information Available: Text giving experimental procedures for product studies and kinetic measurements, product identification, and detailed kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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