9798 *J. Am. Chem. Soc.* **1996,** *118,* 9798−9799

# The Mechanism of Addition of Phenols to Tetramesityldisilene. Evidence for Both Nucleophilic and Electrophilic Rate-Determining Steps

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*Received May 23, 1996*

Following the synthesis of the first stable disilene, tetramesityldisilene (**1**), in 1981,[1] many reactions of disilenes have been chronicled.[2] However, information about the mechanisms of these reactions is still rather scarce. One of the most studied mechanisms is that of the 1,2-addition reaction of alcohols to the Si═Si bond, but also this mechanism is not fully understood.[2] Addition of alcohols to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene gives a 1:1 mixture of the two diastereoisomeric alkoxysilanes, suggesting a stepwise mechanism involving a zwitterionic intermediate.[3] In contrast, theoretical calculations (at the RHF/6-31G* level) predicted a four-center concerted transition state, leading to *syn*-addition, for the gas-phase addition of water to disilene.[4] In agreement, Sekiguchi, Maruki, and Sakurai (SMS) found recently that the addition of 2-propanol and of *tert*-butyl alcohol to the transient disilenes (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilene occurs with high *syn*-diastereoselectivity.[5] With ethanol the addition occurs with high *syn*-diastereoselectivity at low ethanol concentrations, but at a high ethanol concentration a 1:1 mixture of the addition diastereoisomers was obtained. No significant kinetic deuterium isotope effect was found when ethanol-$d_1$ was used. SMS concluded that the rate-determining step of the addition reaction involves a nucleophilic attack of the alcoholic oxygen on the coordinatively unsaturated silicon center, forming a four-membered intermediate which reacts further, either intramolecularly to give *syn*-addition products or intermolecularly (at high alcohol concentrations) to give *anti*-addition products.[5] This contrasts with the common addition mechanism to olefins, which generally involves a rate-determining electrophilic step.

To gain further insight into the mechanism of alcohol addition reactions to disilenes, we have carried out the first Hammett-type[6] study for compounds with multiple bonds to silicon. We studied the kinetics of the addition reactions of seven *para*- and *meta*-substituted phenols to **1**. The resulting Hammett plot has a concave shape with a minimum for phenol, indicating a *change in mechanism from a rate-determining nucleophilic step for electron-rich phenols, to a rate-determining electrophilic step for electron-poor phenols*. Kinetic isotope effect measurements support this interpretation.

The kinetics of the addition of phenols to **1** was followed spectroscopically by measuring the decay rate of the absorption at 420 nm (corresponding to the Si═Si bond in **1**[1]).[7] A large access of the phenol (i.e., 50−6000-fold larger than that used for **1**) was used to enforce pseudo-first-order kinetics. Plots of the pseudo-first-order rate constants ($k_{obs}$) vs phenol concentrations are shown in Figure 1.[8] The excellent correlations between the experimental measurements and first-order kinetics and the linear correlations in Figure 1 imply that the addition reactions are indeed first order in both the disilene and the phenol.[9] The second-order rate constants $k$ for the addition of the various phenols to **1** derived from Figure 1 are summarized in Table 1.[10] Comparison with the results of SMS shows that the rate of addition of phenols to **1** ($k \approx 10^{-4}-10^{-2}$ M$^{-1}$ s$^{-1}$) are much slower compared with the rates of addition of alkyl alcohols to (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilene and 1,2,2-trimethyl-1-phenyldisilene ($k \approx 10^{7}-10^{8}$ M$^{-1}$ s$^{-1}$).[5] The larger steric bulk of the mesityl substituents in **1** may account for this large reactivity difference.

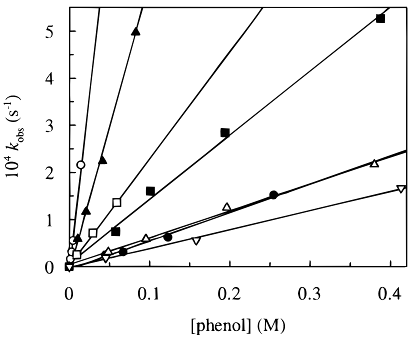

**Figure 1.** Plots of $k_{obs}$ vs [phenol] concentration; *m*,*m*-$(F_3C)_2$-$C_6H_3$-OH (○), *p*-$F_3C$-$C_6H_4$-OH (□), *m*-$CH_3O$-$C_6H_4$-OH (●), $C_6H_5$-OH (▽), *p*-$CH_3$-$C_6H_4$-OH (△), *p*-$CH_3O$-$C_6H_4$-OH (■), *p*-$(CH_3)_2N$-$C_6H_4$-OH (▲).

A Hammett plot of $\log(k_X/k_H)$ vs $\sigma$ (eq 1),[6] where $k_X$ and $k_H$ are the second-order rate constants for the addition to **1** of the substituted and the nonsubstituted phenols, respectively (Table 1), is shown in Figure 2.

$$\log(k_X/k_H) = \rho\sigma \qquad (1)$$

The Hammett plot has a concave shape with a minimum for X = H (i.e., all phenols, either with electron-donating or

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(1) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(2) For recent reviews on disilenes, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (c) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 2. (e) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (f) Raabe, G.; Michl, *J. Chem. Rev.* **1985**, *85*, 419. (g) West, R. *Pure Appl. Chem.* **1984**, *56*, 163.

(3) De Young, D. J.; Fink, M. J.; West, R.; Michl, J. *Main Group Met. Chem.* **1987**, *10*, 19.

(4) Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H., Jr., Schaefer, H. F., III, Morokuma, K., Eds.; Reidel: Dordrecht, The Netherlands, 1986.

(5) Sekiguchi, A.; Maruki, I.; Sakurai, H. *J. Am. Chem. Soc.* **1993,** *115*, 11460.

(6) (a) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96. (b) Johnson, C. D. *The Hammett Equation*; Cambridge University Press: Cambridge, 1973.

(7) $Mes_2Si{=}SiMes_2$ was prepared as described by Tan et al. (Tan, R. P.; Gillette, G. R.; Yokelson, H. B.; West, R. *Inorg. Synth.* **1992**, *29*, 19). The phenols used are commercially available, except for *p*-$Me_2N$-$C_6H_4$-OH which was prepared according to Bordwell (Bordwell, F. G.; Boutan, P. J. *J. Am. Chem. Soc.* **1956,** *78*, 87). The addition products, were isolated on a precoated TLC plate (0.5 mm silica gel F-254) using 15% $CH_2Cl_2$: 85% hexane as the eluent and were characterized by $^1$H NMR and HR-MS or CI-MS. All experiments were performed in oven-dried glassware under vacuum using Schlenk techniques. The kinetic experiments were followed by a HP 8452A diode-array spectrophotometer and were carried out in deoxygenated dry benzene at 75 °C, in a cuvette sealed under vacuum, using an especially designed glassware apparatus (which will be described elsewhere). $^1$H NMR spectra were collected at the end of the kinetic measurements, to verify that the addition products were obtained (e.g., production of the corresponding silanol would indicate the presence of water).

(8) All lines were constrained to intercept the axes at $k_{obs} = 0$ and [phenol] = 0. In all cases excellent correlations with $r > 0.999$ were observed, except for *m*,*m*-$CF_3$ and *m*-$CH_3O$ where $r = 0.994$ and 0.997, respectively.

(9) (a) In $CCl_4$ phenols exist as an equilibrium mixture of monomers, dimers, and trimers (see refs 9b and 9c), and it is reasonable to assume that the same applies to benzene. The observed first-order kinetics in the phenol suggests that the dimer (or trimer) forms of the phenols are not involved in the rate-determining step. (b) Seidel, H.; Ritter, Ch.; Fruwert, J.; Geiseler, G. *Spectrochim. Acta* **1976**, *32A*, 705. (c) Lessinger, L. *J. Chem. Educ.* **1995**, *72*, 85 and references therein.

(10) Since phenols are probably associated to some degree in benzene,[9] the actual concentrations of the phenols are probably lower than those used in Figure 1. Since data for the association constants of phenols in benzene are not available,[9] no corrections in the second-order rate constants $k$ could be made. However, the range of the known association constants for various phenols in $CCl_4$ at 30 °C [9b] suggests that corrections for phenol association will not cause a qualitative change in the Hammett plot.

S0002-7863(96)01746-5 CCC: $12.00

**Table 1.** Second-Order Rate Constants $k$ and $\log(k_X/k_H)$ for the Reactions of Substituted Phenols with **1**[a]

| phenol | $10^4\,k \pm$ SD ($M^{-1}\,s^{-1}$)[b] | $\log(k_X/k_H)$ | $\sigma$[c] |
|---|---|---|---|
| $m,m$-$(F_3C)_2$-$C_6H_3$-OH | 141 ± 8 | 1.55 | 0.88 |
| $p$-$F_3C$-$C_6H_4$-OH | 23.2 ± 0.4 | 0.76 | 0.54 |
| $m$-$CH_3O$-$C_6H_4$-OH | 5.7 ± 0.2 | 0.15 | 0.11 |
| $C_6H_5$-OH | 4.0 ± 0.1 | 0.00 | 0.00 |
| $p$-$CH_3$-$C_6H_4$-OH | 5.9 ± 0.2 | 0.17 | −0.16 |
| $p$-$CH_3O$-$C_6H_4$-OH | 13.9 ± 0.3 | 0.54 | −0.29 |
| $p$-$(CH_3)_2N$-$C_6H_4$-OH | 60.8 ± 0.7 | 1.18 | −0.69 |
| $p$-$F_3C$-$C_6H_4$-OD[d] | 4.4 ± 0.3 | | |
| $p$-$CH_3O$-$C_6H_4$-OD[d] | 19.6 ± 0.5 | | |

[a] In degassed dried benzene at 75 °C. [b] The slope of the linear lines in Figure 1.[10] SD = standard deviation. [c] Shorter, J. *Aust. J. Chem.* **1995**, *48*, 1453. For $p$-$CF_3$, see: Exner, O. In *Correlation Analyses in Chemistry: Recent Advances*; Chapman, N. D., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10. [d] According to $^1H$ NMR, ≥95% D.

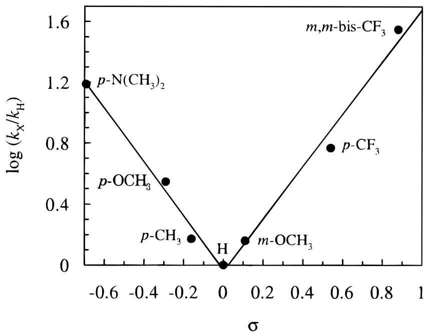
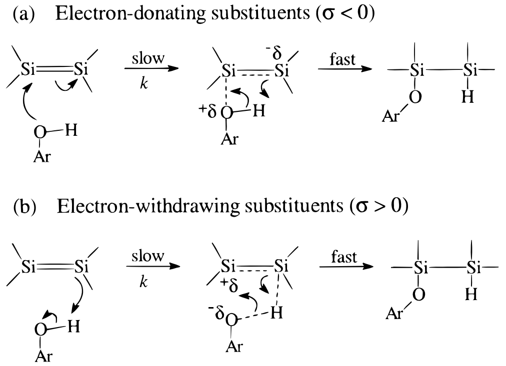


**Figure 2.** A Hammett plot for the reaction of substituted phenols with **1**.

electron-withdrawing substituents, react faster than the parent PhOH (Table 1)). This concave shape is formed by two intersecting straight lines having $\rho$ values with opposite signs. For electron-donating substituents $\rho = -1.77$ ($r = 0.993$),[11] indicating that a positive charge (relative to that in the isolated phenol) is developing on the phenolic oxygen in the transition state of the rate-determining step (Scheme 1a). In contrast, with electron-withdrawing substituents $\rho = 1.72$ ($r = 0.992$),[12] indicating that a negative charge (relative to that in the isolated phenol) develops on the phenolic oxygen in the transition state of the rate-determining step (Scheme 1b). Unfortunately, $\rho$ values for related reactions (such as nucleophilic oxygen attack at a saturated silicon center) are not available, and therefore more quantitative estimates of the charges being developed in the transition states cannot be made. The break in the Hammett plot points strongly to a change in mechanism as a function of the substituent on the phenol: *from a rate-determining nucleophilic step (followed by H transfer), in the case of electron-donating substituents, to a rate-determining electophilic step in the case of electron-withdrawing substituents* (Scheme 1). We are not aware of an analogous case with alkenes. This interpretation is consistent with the relatively low HOMO−LUMO gap in disilenes compared with that for alkenes.[2e,13,14] Phenol association cannot account for the concave Hammett plot, since a linear relationship exists between the association constants (in $CCl_4$) of substituted phenols and the Hammett $\sigma$ values of the substituents.[9b]

**Scheme 1.** Schematic Mechanisms for the Addition Reactions of Substituted Phenols to Disilene **1**


(a) Electron-donating substituents (σ < 0)

(b) Electron-withdrawing substituents (σ > 0)

The measured isotope effects with deuterated phenols (Table 1) also support the mechanisms proposed in Scheme 1. The small $k_H/k_D$ isotope effect of 0.71, measured in the addition of $p$-$CH_3O$-$C_6H_4$-OD to **1**, is fully consistent with a rate-determining nucleophilic attack.[15] The large $k_H/k_D$ isotope effect of 5.27, measured in the addition of $p$-$CF_3$-$C_6H_4$-OD to **1**, strongly supports a mechanism in which a phenolic H (or D) is transferred to **1** in the rate-determining step.[16] Since **1** is a symmetric molecule, the diastereoselectivity of the addition reactions could not be studied and therefore intra- vs intermolecular H-transfer could not be distinguished. Additional studies, including studies of the diastereoselectivity of the addition of electron-rich and of electron-poor phenols to nonsymmetrical disilenes, are in progress.

In summary, the rate-determining step in the addition of phenols to tetramesityldisilene depends on the phenolic substituent: being nucleophilic for electron-donating substituents and electrophilic for electron-withdrawing substituents. Similar studies with other disilenes are needed to generalize our findings.

**Acknowledgment.** This paper is dedicated to Professor Zvi Rappoport (Hebrew University, Jerusalem) on the occasion of his 60th birthday. We thank Prof. Robert West for a generous donation of **1** during the initial stages of this work and for insightful discussions. We are grateful to the US-Israel Binational Fund (BSF) for financial support.

JA961746T

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(11) Correlation of $\log(k_X/k_H)$ vs $\sigma^{+}$ [6b] leads to a better correlation ($r = 0.999$) with $\rho = -0.71$. Note however that "through-resonance", as in the cumyl carbenium ion,[6b] is not possible in this case.

(12) Correlation of $\log(k_X/k_H)$ vs $\sigma^{-}$ [6b] leads to a poorer correlation ($r = 0.982$) with $\rho = 1.67$. Note that $\sigma^{-}$ is different from $\sigma$ only for $p$-$CF_3$.

(13) Shepherd, B. D.; West, R. *Chem. Lett.* **1988**, 183.

(14) With low HOMO−LUMO gaps, both orbitals can interact effectively with the incoming reagent and thus small changes (e.g., in the phenol nucleophilicity) may change the rate-determining step from nucleophilic (i.e., interaction with LUMO (disilene)) to electrophilic (i.e., interaction with HOMO (disilene)). This change in mechanism is not possible with a high HOMO−LUMO gap as in alkenes.

(15) The fact that $k_H/k_D < 1$ may result from a "steric secondary isotope effect" on going from the reactants to a tight transition state. For a review on "steric isotope effects", see: Carter, R. E.; Melander, L. In *Advances in Physical Organic Chemistry*; Gold, V., Ed; Academic Press: London, 1973; Vol. 10, p 1.

(16) A concerted mechanism is also consistent with the high $k_H/k_D$. On the other hand, the small isotope effect measured with $p$-methoxyphenol points to a stepwise addition with electron-rich phenols.