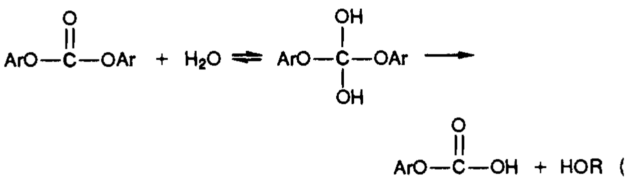
diate is negatively charged (eq 1). At neutral pH, the attacking nucleophile is water, and the intermediate is neutral (eq 4).



$$\mathrm{ArO{-}C({=}O){-}OAr} + \mathrm{H_2O} \rightleftharpoons \mathrm{ArO{-}C(OH)_2{-}OAr} \longrightarrow \mathrm{ArO{-}C({=}O){-}OH} + \mathrm{HOR} \quad (4)$$

Alkaline Hydrolysis. The alkaline hydrolysis of diaryl carbonates, like the alkaline hydrolysis of other esters, is expected to occur by a mechanism involving a tetrahedral intermediate in which formation of the intermediate is rate-determining. Substituent effects for hydrolysis of meta-substituted diphenyl carbonates (ρ = 2.7 for two substituents[16b]) are like those seen for leaving groups in the alkaline hydrolysis of phenyl acetates[10] (ρ = +1.1) and phenyl benzoates[7,8] (ρ = +1.2 to +1.5). Rate-determining addition of hydroxide is logical for aryl carbonates, since the tetrahedral intermediate should eliminate phenoxide more easily than hydroxide and no proton transfers are required within the tetrahedral intermediate.

The three substituents studied in this work (H, p-OCH_3, p-NO_2) span a range of 1.1 in σ values[18] and a range of 5000-fold in alkaline hydrolysis rates. However, the carbon isotope effects are large and span only a small range. The isotope effect increases slightly with decreasing reactivity. This small variation with substituent suggests that, whereas transition-state energy (and thus, reaction rate) is substantially affected by substituent, transition-state structure (and thus, isotope effect) is not; instead, the degree of C–O bond formation at the transition state seems to be nearly constant.

Neutral Hydrolysis. The substituent effects on reaction rates observed in the present study are consistent with those reported previously for the neutral hydrolysis of meta-substituted aryl carbonates.[16b] The range of substituents studied here causes only a 6-fold change in the hydrolysis rate. The carbon isotope effects are slightly larger than those for the alkaline hydrolysis, suggesting that the transition state is later for the alkaline hydrolysis, as expected from structure–reactivity considerations.[19] Isotope effects are available for only two substituents, and no experimentally significant trend with substituent is apparent. It is not clear whether in this case the formation of the tetrahedral intermediate is entirely rate-determining.

Throughout our discussion we have ignored the possibility of a concerted mechanism in favor of the widely accepted stepwise mechanism. Future planned experiments to measure the acyl oxygen and carbonyl oxygen isotope effects by the remote label procedure will afford the opportunity to consider the importance of the concerted mechanism and will allow a more complete characterization of the transition states for these reactions.

---

[18] March, J. *Advanced Organic Chemistry*; John Wiley and Sons: New York, 1985; p 244.

[19] Hammond, G. S. *J. Am. Chem. Soc.* **1959**, *77*, 334.

On the Mechanism of Metal Colloid Catalyzed Hydrosilylation: Proposed Explanations for Electronic Effects and Oxygen Cocatalysis

Larry N. Lewis

Contribution from the General Electric Research and Development Center, P.O. Box 8, Schenectady, New York 12301. *Received October 6, 1989*

Abstract: Several aspects of the platinum-catalyzed hydrosilylation reaction, $R_3SiH + R'CH{=}CH_2$, are described and a mechanism based on the intermediacy of colloids is proposed. New features of this mechanism include (1) formation of a Pt colloid/R_3SiH intermediate **2** from the reaction of the Pt colloid **1** and R_3SiH, (2) consideration of the olefin as a nucleophile and thus intermediate **2** being an electrophile in this reaction, (3) hydrosilylation dependence on cocatalysis by dioxygen where no O–O bond breakage occurs and dioxygen action to electronically modify **2** by making it more electrophilic, (4) hydrosilylation being but one case of the reactivity of **2** with nucleophiles; the reaction with R″OH where R″ = H or alkyl is discussed. The effect of the electronic nature of the substituents on the rate of hydrosilylation was measured. Electron withdrawing substituents, R, on R_3SiH accelerate the rate of addition to olefins, e.g. the rate of addition of $(EtO)_3SiH$ to olefins proceeds at a higher rate than the addition of Et_3SiH to olefins. Electron donating groups, R′, on $R'CH{=}CH_2$ greatly accelerate the rate of R_3SiH to olefins, e.g. the Et_3SiH addition occurs at a faster rate to $Me_3SiCH{=}CH_2$ than to $Cl_3SiCH{=}CH_2$. The relative rate of addition of $(EtO)_3SiH$ to a series of para-substituted styrenes was studied which confirmed the trend that higher rates of addition of R_3SiH occurs to olefins, $R'CH{=}CH_2$ with more electron donating substituents, R′. The origin of the cocatalytic effect of dioxygen in hydrosilylation was studied by generating Pt colloid under an atmosphere containing $^{16}O_2$ and $^{18}O_2$ and noting that the O–O bond is not broken and reformed under these conditions. It was demonstrated that the proposed intermediate **2** behaves as an electrophile by showing that $Me_3SiCH_2CH{=}CH_2$ exchanges with Et_3SiH in the presence of Pt to give trapped products based on the rearranged products Me_3SiH and $Et_3SiCH_2CH{=}CH_2$ in the presence of an electrophile (in this case Pt/Et_3SiH). The reaction of water with R_3SiH in the presence of a Pt catalyst in commercial silicone foams produces H_2, and this reaction is described in the context of hydrosilylation where the water nucleophile replaces the olefin.

Introduction

In 1986 we reported that the key event in the Pt-catalyzed hydrosilylation reaction, eq 1, was formation of Pt colloid.[1] The well-known induction period and formation of the characteristic yellow color in this reaction were directly linked to the formation of the colloid. No evidence for molecular species was found and

$$R_3SiH + H_2C{=}CHR' \xrightarrow{\text{catalyst}} R'CH_2CH_2SiR_3 \qquad (1)$$

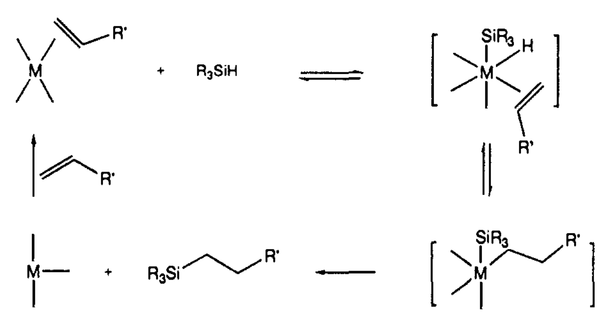
direct evidence for colloid formation was presented; thus colloids were implicated as the catalytic species in this reaction. Since

---

[1] Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

0002-7863/90/1512-5998$02.50/0 © 1990 American Chemical Society

Scheme I



- Metal (M)/olefin complexes are catalyst precursors
- Some metal/silyl complexes are catalyst precursors

that time, we have described our additional efforts to synthesize and characterize colloids of the platinum group. Additional data showed that low-valent Pt species were present under conditions of hydrosilylation, e.g. from the reaction of a platinum salt or compound with an SiH compound.[2]

Many aspects of the mechanism of the Pt catalyzed hydrosilylation reaction remain unclear. Scheme I represents the "accepted" Chalk–Harrod mechanism which follows traditional tenets of organometallic chemistry.[3] This mechanism attempts to not only account for the events in eq 1, but also for the many observed side reactions including olefin isomerization, oligomerization, and reduction. In their own discussion on objections to their mechanism, Chalk and Harrod report that in the reaction between chloroplatinic acid and $(EtO)_3SiH$ a yellow color forms "as usual". Chalk and Harrod also describe the requirement for oxygen in hydrosilylation.

Our recent work further supports the intermediacy of colloids in hydrosilylation; colloid formation is responsible for the yellow color alluded to by Chalk and Harrod.[2,6] We and others have also described the so called oxygen effect.[7,8] No explanation for this effect has been offered.

This report describes new observations with regard to the platinum-catalyzed hydrosilylation reaction. Platinum colloids are assumed to be the catalytic intermediate in these reactions. There are, no doubt, authentic homogeneous catalysts for hydrosilylation, e.g. the molecular compounds such as those proposed in Scheme I are actually formed. However, under conditions in this report, where there are weakly coordinated ligands to platinum or ligands that can be removed via reduction, metal colloids form under the reducing conditions of the reaction.

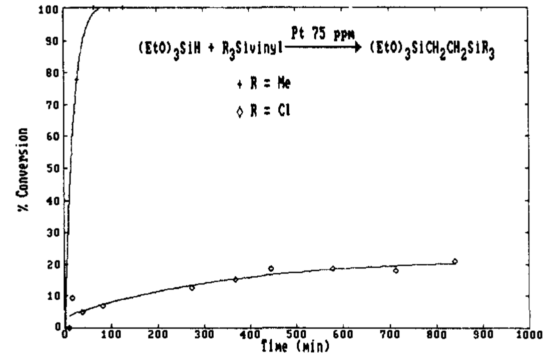


Figure 1. Relative rate of addition of $(EtO)_3SiH$ to $Me_3Si(vinyl)$ and $Cl_3Si(vinyl)$, 5.4 mmol SiH and olefin, 1.03 mmol decane internal standard, and 0.6 μmol Pt (see Experimental Section).

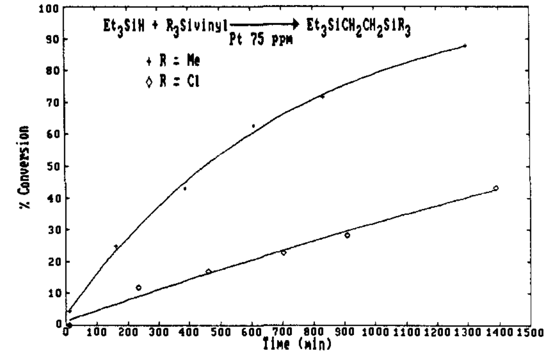
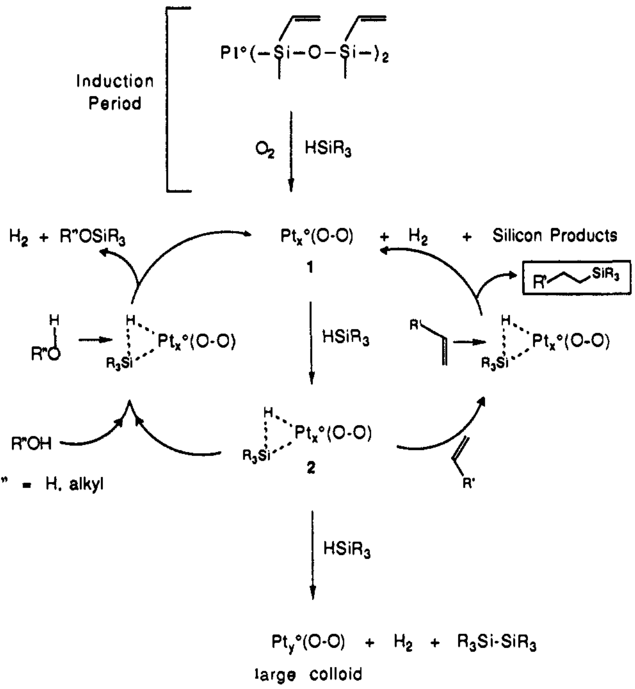


Figure 2. Relative rate of addition of Et_3SiH to $Me_3Si(vinyl)$ and $Cl_3Si(vinyl)$, 10.8 mmol SiH and 11.4 mmol olefin, 1.03 mmol decane internal standard, 0.6 μmol Pt (see Experimental Section).

Scheme II



Results and Discussion

Proposed Mechanism. Scheme II is a proposed mechanism for the platinum-catalyzed hydrosilylation reaction. The events which occur during the induction period have been addressed previously,[1] where the so-called Karstedt's platinum catalyst[9,10] reacts with R_3SiH to give H_2, hydrosilylated ligand, and platinum colloid **1**. One could substitute $Pt_{colloid}$ for the molecular complex of Scheme I and the mechanisms would then proceed in the same way. The new features in Scheme II beyond the induction period (colloid formation) are (1) formation of **2** from **1** where here attack by R_3SiH precedes attack of the olefin (opposite that of Scheme I), (2) treatment of the attacking olefin as a nucleophile (complex **2** is therefore an electrophile), (3) bonding of O_2 to the active catalyst species but acting as a true co-catalyst (oxygen is not consumed in the reaction), (4) generalization of the mechanism for attack of **2** by nucleophiles such as R″OH, where R″OH can be water or alcohols.

Electronic Factors and Their Effect on Rate. Extensive reviews of the hydrosilylation reaction show that electron withdrawing

---

(2) Lewis, L. N.; Lewis, N. *Chemistry Mater.* **1989**, *1*, 106.

(3) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; John Wiley: New York, 1977; p 673.

(4) Armitage, D. A. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, p 117.

(5) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

(6) (a) Lewis, L. N.; Uriarte, R. J.; Lewis, N. *J. Mol. Cat.*, submitted for publication. (b) Lewis, L. N.; Uriate, R. J.; Lewis, N. *J. Catal.*, submitted for publication.

(7) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.

(8) Onopchenko, A.; Sabourin, E. T. *J. Org. Chem.* **1987**, *52*, 4118.

(9) Karstedt, B. D. U.S. Patent 3,775,452, 1973.

(10) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191.

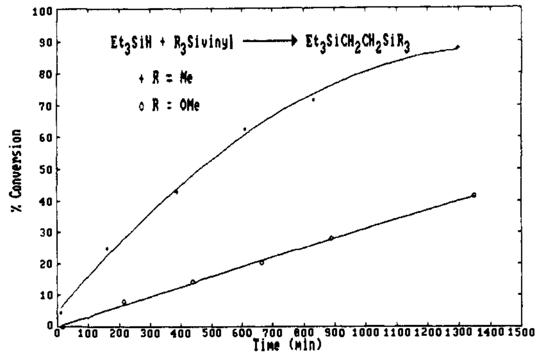
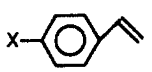


Figure 3. Relative rate of addition of Et_3SiH to Me_3Si(vinyl) and $(MeO)_3Si$(vinyl) (see Figure 2 and Experimental Section).

Table I. Percent Conversion for the Reaction[a] of $(EtO)_3SiH$ with Various Styrenes



X	% conversion
H	79.6
Me	99.7
OMe	68.6
Cl	58.0

[a] Reaction run at ambient temperature, 75 ppm Pt, 70 h, decane internal standard.

substituents on R in eq 1 increase the rate of addition to olefins relative to electron donating R groups.[3,11-13] An example of this trend is the much higher rates of addition to terminal olefins for $(EtO)_3SiH$ and Cl_3SiH vs Et_3SiH.

There have been very few reports on the effect of substituents on the olefin (R′ in eq 1) on rates of addition of SiH compounds. In one study, it was shown that as the amount of halide substitution increased, the rate of hydrosilylation decreased. For addition of $MeCl_2SiH$: $H_2C{=}CH_2 > CH_2C{=}CF_2 > F_2C{=}CFCl > F_2C{=}CF_2$.[13] These results are supported by at least one other study,[14] and these trends are consistent with higher rates of addition corresponding to more nucleophilic olefins. The effect of increased rate of addition for an SiH compound for more nucleophilic olefins is illustrated in Figures 1–3. Figure 1 shows that the addition of $(EtO)_3SiH$ proceeded at a faster rate to the more nucleophilic olefin, Me_3Si(vinyl), than to the less nucleophilic olefin, Cl_3Si(vinyl). Figure 2 shows the same trend as Figure 1, except where Et_3SiH was used in place of $(EtO)_3SiH$. Note that the addition of Et_3SiH to an olefin proceeded at a slower rate than the addition of $(EtO)_3SiH$ to the same olefin. This latter trend confirms the proposal that higher hydrosilylation rates are achieved with more electron withdrawing groups on R_3SiH compared to R_3SiH with more electron donating groups. In Figure 3, the relative rate of addition of Et_3SiH was shown to go at a faster rate to Me_3Si(vinyl)(more nucleophilic) than to $(MeO)_3Si$(vinyl).

A further probe of the effect of olefin nucleophilicity on the rates of addition of SiH compounds was made by using para-substituted styrenes. Addition of SiH compounds to styrenes went at a slower rate than addition to the vinylsilicon compounds (Figure 1, supplementary material). The relative activity for the addition of $(EtO)_3SiH$ to four different styrenes were measured p-$H_2C{=}CHC_6H_4X$, X = H, Me, OMe, and Cl. As shown in Table I, the relative rates of addition followed the trend for X: Me > H > OMe > Cl.[15-17]

The Oxygen Effect. It was established that the well-known induction period in Pt-catalyzed hydrosilylation corresponded to the formation of Pt colloid from molecular precursors.[1] We found that colloid formation itself did not occur in the absence of oxygen.[2] We recently reported the direct synthesis of platinum group metal colloids via reaction of metal halide salts with SiH compounds, for example the addition of $PtCl_4$ to $HMe_2SiOSiMe_2H$ gave gas evolution with formation of Pt colloid with the characteristic yellow color. No reaction occurred in the strict absence of oxygen (eq 2).

$$PtCl_4 + HMe_2SiOSiMe_2H \text{ (100-fold excess)} \rightarrow Pt_{colloid} + H_2 + HMe_2Si(OMe_2Si)_xOSiMe_2H \quad (2)$$

$$x = 0\text{–}6 \text{ (GCMS detection)}$$

In our previous work on colloid formation,[1,2] we showed the Pt-catalyzed formation of H_2 from R_3SiH (about 10–100 turnovers). The reaction stopped and required O_2 but the origin of cessation and O_2 cocatalysis were not previously addressed. The Cl from $PtCl_4$ presumably ends up as SiCl as described earlier.[1]

The solution from eq 2 which contained $Pt_{colloid}$ was stirred 12 h under an atmosphere consisting of equal molar amounts of $^{18}O_2$ and $^{16}O_2$ with Ar as an internal standard. Analysis of the gases by mass spectroscopy showed no oxygen scrambling; $^{16}O_2$ and $^{18}O_2$ at masses 32 and 36 amu were observed, but no mass 34 (which would correspond to $^{18}O^{16}O$) was observed. In a separate experiment, the colloid forming eq 2 was repeated under an atmosphere containing $^{18}O_2$ and $^{16}O_2$. After the H_2 evolution was complete, the gases were analyzed by mass spectroscopy and again no evidence for the scrambled dioxygen was found at mass 34.

The oxygen effect in hydrosilylation has been discussed in some detail by Harrod and Chalk.[3] Hydrosilylation is truly catalytic in oxygen in that oxygen is neither consumed nor does it end up in the product, despite the fact that silicon is quite oxophilic. The results with $^{16}O_2/^{18}O_2$ mixtures show that O–O bond breakage and reformation does not occur in the colloid forming reaction. These results imply, therefore, that O–O bond breakage does not occur in hydrosilylation.

In the absence of oxygen or when a reaction in progress becomes depleted in oxygen, it is a typical observation that the reaction stops and an ever deepening brown color forms. Under these conditions, the darker color is due to larger and larger colloid formation.[6] Thus one function of oxygen is to prevent irreversible colloid agglomeration; larger particle size colloids have reduced activity. A second role for oxygen may be to make the Pt/SiH complex, **2** from Scheme I, more prone to nucleophilic attack by olefin, e.g. addition of O_2 to **2** makes the complex **2**/O_2 more electrophilic than **2** alone. An alternative role of O_2 may simply be to act as a weak ligand, holding a coordination site between hydrosilylation cycles. An example of this kind of role for dioxygen on rhodium has recently been reported.[18] Our TEM/X-ray spectroscopic studies[2,6] showed that Si and O always are present in the Pt colloids. Our earlier EXAFS work[2] is now continuing in order to address oxygen's role in more detail.

Electrophilic Nature of Proposed Pt/R_3Si–H Complex 2. To test whether complex 2 would behave as an electrophile as proposed, the general reaction of eq 3 was investigated, where E–N in this case is a R_3SiH compound.[19,20] In order to test this idea,

$$Me_3SiCH_2CH{=}CH_2 + E\text{–}N \rightarrow H_2C{=}CHCH_2E + Me_3Si\text{–}N \quad (3)$$

---

(11) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17* 407.

(12) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. In *J. Organomet. Chem. Library*; Seyferth, D., Ed.; Elsevier: Amsterdam 1977; Vol. 5.

(13) Eaborn, C.; Bott, R. W. In *The Bond to Carbon*; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1.

(14) Sheludyakov, V. D.; Zhun, V. I.; Vasenko, S. D.; Bochkarev, T. F.; Turkel'taub, G. N.; Kisin, A. V.; Nosova, V. M. *Zh. Obshch. Khim.* **1985**, *55*, 1544.

(15) A rough Hammett plot of σ (for Me, H, Cl) vs log % conversion X/% conversion H had a negative slope consistent with an acceleration of rate due to electron donation. Furthermore, the % conversion for OMe can only be considered by employing σ induction values, thus resonance appeared to have a small effect on this reaction. Future work will evaluate the relative rates of meta substituted styrenes.

(16) Isaacs, N. S. *Physical Organic Chemistry*, Longman Scientific & Technical: Essex, England, 1987; pp 129 ff.

(17) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A*; Plenum: New York, 1980.

(18) Cannon, K. C.; Jo, S. K.; White, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 5069.

the Pt-catalyzed hydrosilylation reaction between an allyl silicon compound and R_3SiH was monitored in order to see if any evidence for the rearrangement products of eq 3 could be found. The formation of π allyl-metal complexes is well known, but no evidence for an Pt π allyl complex formation was noted (NMR). One problem with this approach was the fact that some hydrosilylation reactions proceed at such a high rate that only hydrosilylation products were observed. Thus the reaction between $(EtO)_3SiH$ and $(MeO)_3SiCH_2CH{=}CH_2$ gave only addition product $(EtO)_3Si(CH_2)_3Si(OMe)_3$ as monitored by gas chromatography/mass spectroscopy (GCMS). A less reactive SiH (Et_3SiH in place of $(EtO)_3SiH$) source was employed to slow down the hydrosilylation reaction. The reaction of eq 4 was monitored by GCMS and showed the predicted hydrosilylation product as the major species. In addition, minor products due to the electrophilic attack and rearrangement of the $(MeO)_3SiCH_2CH{=}CH_2$ compound with Et_3SiH were observed. These included the $Et_3SiCH_2CH{=}CH_2$ species itself and the subsequent hydrosilylation product of Et_3SiH with $Et_3SiCH_2CH{=}CH_2$; no $(MeO)_3SiH$ was observed.

$$(MeO)_3SiCH_2CH{=}CH_2 + Et_3SiH \xrightarrow{Pt} \underset{\text{major}}{(MeO)_3Si(CH_2)_3SiEt_3} + \underset{\text{minor}}{Et_3SiCH_2CH{=}CH_2 + Et_3Si(CH_2)_3SiEt_3} \quad (4)$$

A more dramatic example of this electrophilic allylic rearrangement was found in the reaction of eq 5. The major species was that due to normal hydrosilylation **3**. However there was about 10% yield (by GC) of the two minor products **4** and **5**.

$$Me_3SiCH_2CH{=}CH_2 + Et_3SiH \xrightarrow{Pt} \underset{\substack{\mathbf{3}\\ \text{major}}}{Me_3Si(CH_2)_3SiEt_3} + \underset{\text{minor}}{\underset{\mathbf{4}}{Me_3Si(CH_2)_3SiMe_3} + \underset{\mathbf{5}}{Et_3Si(CH_2)_3SiEt_3}} \quad (5)$$

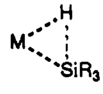
These latter two products are consistent with the rearrangement reaction of eq 3 which would form $Et_3SiCH_2CH{=}CH_2$ and Me_3SiH. The observed products in eq 5 are from SiH additions: Me_3SiH plus starting $Me_3SiCH_2CH{=}CH_2$, to give **4**, and $Et_3SiCH_2CH{=}CH_2$ plus starting Et_3SiH, to give **5**. The addition product **3** was isolated by distillation from the reaction mixture in eq 5 and then combined with platinum in two different forms in order to see if the other two products, **4** and **5**, were from platinum-catalyzed rearrangement of **3**. Thus in one experiment, **3** was combined with Karstedt's platinum catalyst and allowed to stand overnight. In a second experiment, **3** was combined with Karstedt's platinum catalyst and $(EtO)_3SiH$ in order to preform Pt colloid,[1] and this combination was allowed to stand overnight. In neither case were the products attributed to electrophilic rearrangement, **4** and **5**, observed. These latter results confirm that the origin of the products of eq 5 are not due to reaction of the addition product **3** with Pt in any of the forms encountered in the hydrosilylation reaction. Moreover, they are not due to some chemistry in the injector region of the GC. Speier has described analogous chemistry to that described in eq 3 where allyl is replaced by vinyl.[11]

Other Nucleophiles. The mechanism in Scheme II suggests that there is a common intermediate for the hydrosilylation reaction (**2** + olefin) and the reaction with other nucleophiles such as water or alcohol. Luo and Crabtree recently described their work on the reaction between alcohols and R_3SiH compounds catalyzed by iridium.[21] The platinum-catalyzed reaction of water or alcohols with R_3SiH compounds to produce hydrogen has been employed industrially for over 20 years.[22] For example, a silicone foam is generated by combining vinyl silicones, SiH-containing silicones, platinum, and water or alcohol. Platinum catalyzes the hydrosilylation of the two silicones which in this case form a crosslinked three-dimensional network. In addition, platinum catalyzes the reaction between SiH and water to produce H_2. This hydrogen is released during formation of the crosslinked network so that a foamed silicone product is generated. We collected and analyzed the gases (by mass spectroscopy) from a foam reaction using either H_2O or D_2O. In the H_2O case, only H_2 was observed. However, in the D_2O case, both H_2 (from adventitious H_2O) and HD were observed. D_2 was not found, which is consistent with the proposed mechanism in Scheme II where one half of the H_2 formed comes from SiH and the other half comes from the nucleophile. Hydrogenated vinyls were not observed in the foam experiments, which for this system suggested that the hydrosilylation rate was much higher than the hydrogenation rate.

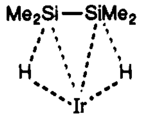
Comparison of Proposed Mechanism to Chalk-Harrod. A key difference between the proposed mechanism in Scheme II and Chalk-Harrod is that in Scheme II the reaction of R_3SiH occurs with platinum first followed by attack by olefin. Only kinetic studies designed to establish the rate-determining step of the hydrosilylation reaction can distinguish between the two proposals.

The Scheme II mechanism suggests that the two key steps in hydrosilylation are the formation of **2** by reaction of R_3SiH with platinum followed by concerted attack by olefin. We recently reported that, contrary to earlier reports by others, the rate of addition to olefins follows $R_3SiH > R_2SiH_2 > RSiH_3$.[7] An explanation for the apparent "poisoning" by R_2SiH_2 and $RSiH_3$ is that the di- and trihydrides chelate to platinum, making their removal more difficult than removal of monohydride. Our observation was that addition of R_2SiH_2 to terminal olefins, $R'CH{=}CH_2$, proceeded very slowly. Analysis showed that when the last trace of R_2SiH_2 was consumed so that only $R_2(R^1CH_2CH_2)SiH$ was present, addition of the second hydrogen to $R'CH{=}CH_2$ went at a faster rate than the first addition, to form $R_2Si(CH_2CH_2R^1)_2$. Thus, it appeared that R_2SiH_2 acted as a poison.

Thus the proposed structure of **2** resembles that proposed for non-classical H_2 coordination.[23,24]



Examples of non-classical SiH to metal bonding included Crabtree's iridium work[21] as well as work by others.[25,26] An example of the proposed "chelated" disilane which inhibits hydrosilylation in platinum has been proposed for iridium.[27]



The inhibition by di- and trisilanes can only be possible if breakage of the metal-SiH bond lies on the rate determining step.

Summary

The proposed mechanism in Scheme II for metal colloid catalyzed hydrosilylation involves the formation of the metal colloid/R_3SiH intermediate **2**. Nucleophilic attack by an olefin on **2** results in hydrosilylation. This proposal explains and is supported by the literature results on electronic effects on substituents on R_3SiH and the olefin. The present work clearly shows that higher rates of addition to olefins are achieved for olefins that contain electron donating groups vs those olefins with less electron donating groups. Bond scission and reformation of the O-O bond in dioxygen did not occur during platinum colloid formation nor was

---

(19) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

(20) Wickham, G.; Young, D.; Kitching, W. *Organometallics* **1988**, *7*, 1187.

(21) Luo, X-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.

(22) (a) Reaction of SiH with H_2O: Modic, F. J. U.S. Patent 4,418,157, 1983. (b) Reaction of SiH with ROH: Kittle, R. E. U.S. Patent 4,026,843, 1977. (c) Reaction of SiH with SiOH: Smith, W. B. U.S. Patent 3,393,705, 1975.

(23) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(24) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 209.

(25) Carre, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 1272.

(26) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

(27) Crabtree, R. H. Personal communication of unpublished results, 1988.

bond scission and reformation observed for dioxygen in the presence of preformed colloid. On the basis of these results and the fact that no oxygen is consumed nor ends up in the silicon products in hydrosilylation, it is proposed that in its role as a cocatalyst, oxygen acts to modify the reactivity of the proposed intermediate **2** without any O–O bond breakage. Oxygen coordination to intermediate **2** would make this intermediate more electrophilic and more prone to attack by nucleophiles. Oxygen also prevents irreversible colloid agglomeration.

It is difficult to determine if olefin (or R″OH) binds to the colloid prior to reaction at the silicon center. There is some evidence that some precoordination occurs. In our work with Rh colloids,[6a] ^{13}C NMR showed ^{13}C–^{103}Rh coupling from the vinyl carbons in cyclo-tetravinyltetramethyltetrasiloxane (D_4^{vinyl}) to Rh in a preformed Rh colloid. In addition, the patent literature has at least one example where D_4^{vinyl} inhibits the rate of Pt-catalyzed hydrosilylation.[28] Nevertheless, formation of intermediate **2** followed by attack of nucleophile (olefin or R″OH) does offer an explanation for the observed electronic phenomena.

Further support for the proposal of an electrophilic intermediate such as **2** came from the study of the rearrangement of allyltrimethylsilane in the presence of Pt and Et_3SiH, eq 5. The observation that allyltrimethylsilane undergoes rearrangement chemistry of the type mediated by an electrophile, e.g. Pt colloid/Et_3SiH intermediate, furthers adds support to the proposed mechanism in Scheme II.

Many presumably anomalous phenomena are explained by the proposals presented here. The origin of the induction period and yellow color have already been ascribed to the colloid formation. The poisoning effect[7] of Pt catalysts by $R_{3-x}SiH_x$ where $x > 1$ may be explained by the chelation of the di- and trisilanes to the Pt colloid, their removal being more difficult than the removal of monosilanes. Large-scale hydrosilylations often are plagued by irreproducible results with formation of dark colors. The origin of the irreproducibility is most likely oxygen defficiency. When intermediate **2** is in an oxygen-free environment, it is not sufficiently electrophilic to react with the weakly nucleophilic olefins, thus colloid agglomeration occurs. Larger particle size Pt colloids give rise to the darker colors and, as we have described earlier,[6] less active catalysts due to the lower surface to volume ratio of the colloid. Finally, the differences in activity between the various platinum group metals[7] are likely due to the electrophilicity and/or ease of formation of the metal colloid/R_3SiH intermediates, e.g. **2** of Scheme II. In addition, the tendency of the other platinum group metals to irreversibly agglomerate instead of forming stable colloids effects their catalytic activity. Thus, in the absence of strongly stabilizing ligands, palladium forms bulk palladium metal under hydrosilylation conditions.[2]

Experimental Section

General. Hydrosilylation reactions were monitored with use of gas chromatography employing a HP model 5890A gas chromatograph with a model 7673A auto sampler, a thermal conductivity detector, and a 6-ft, 3% OV 101 column. ^1H and ^{13}C NMR spectra (all run in $CDCl_3$) were recorded on a GE model QE-300 NMR spectrometer (300.15 MHz and 75.43 MHz, respectively). ^{13}C assignments made used applied proton test (APT). ^{29}Si, ^2D, and some ^{13}C NMR spectra were recorded on a Varian XL 300 NMR spectrometer at 59.3, 46.0, and 75.43 MHz respectively. Chemical shifts (δ) are relative to TMS internal standard.

Raman spectra were obtained with a SPEX Ramalog 10 system using the SPEX sample chamber. The sample holder was a rotating cell built at GE CRD where the laser light enters the cell through the side wall and the scattered radiation exits through the bottom, yielding a 90° scattering geometry. The rotation speed is continuously variable. Scattered light was detected with a photomultiplier operating in the photon counting mode. A SPEX DM1B data system provided the data handling and instrument control. Scans were summed to obtain spectra. Raman excitation was provided by a Spectra Physics Ar ion laser operating at 514 nm. The power head was 300 MW.

GCMS analysis was performed using a Varian Model MAT311A instrument. High-resolution mass spectra (HRMS) were recorded on a VG Analytical Model ZAB-2F gas chromatograph mass spectrometer, run in the accurate mass mode at 5500 resolution. Mass spectra on gas mixtures were recorded on a Varian MAT 731 mass spectrometer.

The platinum catalyst employed in this study was Karstedt Pt catalyst[9] which is a xylene solution containg 5% by weight Pt. This solution delivers 0.26 μmol/μL or 50 μg/μL (available from Petrarch Systems as PC072, their's is 3–3.5% Pt).

Relative rate experiments were carried out by monitoring the disappearance of starting material/appearance of product by GC.

Relative Rate of Addition of $(EtO)_3SiH$ to Me_3Si(vinyl) and Cl_3Si(vinyl) (Figure 1). (a) $(EtO)_3SiH$ (1 mL, 5.4 mmol), Me_3Si(vinyl) (0.83 mL, 5.4 mmol), decane (internal standard, 0.2 mL, 1.03 mmol), and Pt Karstedt catalyst (2.7 μL; 0.13 mg, 0.6 μmol Pt) were combined, and the solution was monitored by GC. For

$(CH_3CH_2O)_3SiCH_2CH_2Si(CH_3)_3$
a b c d e

^1H NMR 3.84 (q, 7 Hz, b), 1.23 (t, 7 Hz, a), 0.53 (s, c,d), −0.1 (s, e); ^{13}C NMR 58.69 (b), 18.74 (a), 8.15 (c), 3.05 (d), −1.93 (e); HRMS ($M^+ - CH_3$) calcd for $C_{10}H_{25}O_3{}^{28}Si_2$ 249.1342, found 249.1337.

(b) The reaction above was repeated except that Cl_3Si(vinyl) (0.7 mL, 5.4 mmol) was substituted for Me_3Si(vinyl) in a. For

$(CH_3CH_2O)_3SiCH_2CH_2SiCl_3$
a b x c d y

^1H NMR 1.24 (t, 7 Hz, a), 1.40 (m, c,d), 3.9 (q, 7 Hz, b); ^{13}C NMR 2.06 (c), 8.37 (d), 18.13 (a), 59.18 (b); ^{29}Si NMR −48 (x), 13.7 (y).

Relative Rate of Addition of Et_3SiH to Me_3Si(vinyl) and Cl_3Si(vinyl) (Figure 2). (a) Et_3SiH (1.72 mL, 10.8 mmol), Me_3Si(vinyl) (1.66 mL, 11.4 mmol), decane (0.2 mL), and Karstedt's platinum catalyst (2.7 μL) were combined, and the solution was monitored by GC. ^1H and ^{13}C NMR identical with those reported previously.[7] HRMS (M^+) calcd for $C_{11}H_{28}{}^{28}Si_2$ 216.1730, found 216.1729.

(b) The reaction in a was repeated except that Cl_3Si(vinyl) (1.54 mL, 11.9 mmol) was used in place of Me_3Si(vinyl). For

$(CH_3CH_2)_3CH_2CH_2SiCl_3$
a b c d

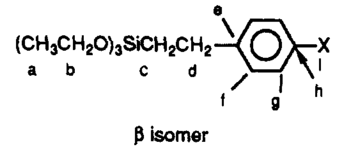
^1H NMR ($CDCl_3$) 0.16 (t, 6 Hz, b), 0.32 (m, c), 0.55 (t, 6 Hz, a), 0.87 (m, d); ^{13}C NMR 2.79 (a), 7.3 (b), 9.15 (c), 13.92 (d).

Relative Rate of Addition of Et_3SiH to Me_3Si(vinyl) and $(MeO)_3Si$(vinyl). The reaction of Et_3SiH and Me_3Si(vinyl) was run as described above. Et_3SiH (1.72 mL, 10.8 mmol), $(MeO)_3Si$(vinyl) (1.66 mL, 11.7 mmol), decane (0.2 mL), and Karstedt's platinum catalyst (2.7 μL) were combined, and the solution was monitored by GC. For

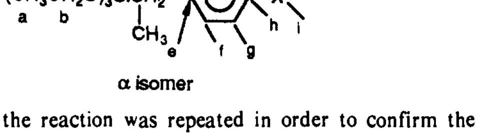
$(CH_3CH_2)_3SiCH_2CH_2Si(OMe)_3$
a b c d e

^1H NMR 0.55 (overlapping m, b,c,d), 0.94 (t, 8 Hz, a), 3.57 (s, e), integral 1:0.97:0.98, calcd (b,c,d):a:e 1:0.9:0.9; ^{13}C NMR 1.04, 1.78 (c,d), 2.57 (b), 7.15 (a), 50.17 (e).

Relative Rate of Addition of $(EtO)_3SiH$ to Styrenes. In all four cases the styrene (26.7 mmol, p-$H_2C{=}CHC_6H_4X$) was combined with $(EtO)_3SiH$ (5 mL, 26.7 mmol), decane (internal standard, 0.5 mL, 2.57 mmol), and Karstedt's platinum catalyst (3.5 μL): X = H, 3.1 mL; X = Me, 3.5 mL; X = OMe, 3.55 mL; X = Cl, 3.2 mL. Reactions were monitored by GC, which showed the presence of two isomers in each case.



β isomer



α isomer

For each styrene the reaction was repeated in order to confirm the identity of the products observed in the GC. For X = H: Integration of the GC products peaks showed 61% β and 39% α, which was verified by proton NMR integration, e.g. the response factors of the two isomers were the same in the GC. β isomer: ^1H NMR 0.99 (CM[29], 17 Hz, 3

---

[28] Maxson, M. T. U.S. Patent 4,785,066, 1988.

[29] There is a characteristic multiplet in these compounds due to the abx_2 spin system which we fondly call a Colborn multiplet (CM), Colborn, R. E. *J. Chem. Educ.* **1990**, *67*, 438.

Hz, c), 1.22 (t, 7 Hz, a), 2.74 (CM, 17 Hz, 3 Hz, d), 3.81 (q, 7 Hz, b), 7.2 (m, f–h); ^{13}C NMR 12.65 (c), 18.30 (a), 29.00 (d), 58.40 (b), 124.87 (f), 125.66 (h), 127.88 (g), 144.64 (e). α isomer: ^{1}H NMR 1.14 (t, 7 Hz, a), 1.42 (d, 8 Hz, d), 2.30 (q, 8 Hz, c), 3.71 (q, 7 Hz, b), 7.2 (m, f–h); ^{13}C NMR 15.66 (c), 18.38 (a), 26.25 (d), 58.81 (b), 124.84 (f), 125.64 (h), 128.32 (g), 144.05 (e). X = CH_3 (p-CH_3 is labeled "i"): 61% β, 39% α. β isomer: ^{1}H NMR 0.97 (CM, 17 Hz, 3 Hz, c), 1.22 (t, 7 Hz, a), 2.29 (s, i), 2.70 (CM, 17 Hz, 3 Hz, d), 3.81 (q, 7 Hz, b), 7.07 (m, f–g); ^{13}C NMR 12.79 (c), 18.31 (a), 20.97 (i), 28.53 (d), 58.40 (b), 127.70, 128.90 (f,g), 134.09 (h), 141.64 (e). α isomer: ^{1}H NMR 1.15 (t, 7 Hz, a), 1.40 (d, 7 Hz, c), 2.28 (i), 2.59 (q, 7 Hz, d), 3.71 (q, 7 Hz, b); ^{13}C NMR 15.83 (c), 18.39 (a), 20.97 (i), 25.67 (d), 58.79 (b), 128.97, 129.0 (f,g), 134.97 (h), 140.88 (e). X = OMe, GC showed only ca. 60% conversion to two products, 66% β and 34% α. β isomer: ^{1}H NMR 0.95 (CM, 17 Hz, 3 Hz, c), 1.22 (t, 7 Hz, a), 2.68 (CM, 17 Hz, 3 Hz, d), 3.70 (i), 3.8 (q, 7 Hz, a), 6.7, 7.1, 7.3 (m, f,g); ^{13}C NMR 13.04 (c), 18.36 (a), 28.19 (d), 55.02 (i), 58.39 (b), 113.81 (f), 128.76 (g), 136.75 (h), 157.88 (e). α isomer: ^{1}H NMR 1.14 (t, 7 Hz, a), 1.38 (d, 8 Hz, d), 2.55 (q, 7 Hz, c), 3.70 (s, i), 3.82 (q, 7 Hz, b); ^{13}C NMR 15.98 (c), 18.43 (a), 25.17 (d), 55.07 (i), 58.79 (b), 111.37 (f), 128.72 (g), 136.00 (h), 157.34 (e). X = Cl, GC shows 40% α, 60% β. β isomer: ^{1}H NMR 0.95 (CM, 17 Hz, 3 Hz, c), 1.22 (t, 7 Hz, a), 2.69 (CM, 17 Hz, 3 Hz, d), 3.82 (q, 7 Hz, b), 7.2 (m, g,h); ^{13}C NMR 12.64 (c), 18.32 (a), 28.46 (d), 58.45 (b), 128.40 (f), 129.24 (g), 131.36 (h), 143.09 (e). α isomer: ^{1}H NMR 1.15 (t, 7 Hz, a), 1.38 (d, 8 Hz, d), 2.26 (q, 7; Hz, c), 3.72 (q, 7 Hz, b), 7.2 (m, g,h) ^{13}C NMR 15.53 (c), 18.32 (a), 25.78 (d), 58.90 (b), 128.14 (f), 129.27 (g), 130.49 (h), 142.73 (e).

Reaction of $PtCl_4$ with $HMe_2SiOSiMe_2H$. $PtCl_4$ (0.1 g, 0.297 mmol) was slowly added to $HMe_2SiOSiMe_2H$ (5 mL, 28.2 mmol), gas evolution was noted, and the characteristic yellow color formed ($Pt_{colloid}$, eq 2). GCMS analysis m/e for $HMe_2SiO(Me_2SiO)_xOSiMe_2H$: ($x$ = 1) 207 (M^+ – H, 67), 193 (M^+ – CH_3, 90), 133 (M^+ – HMe_2SiO, 75); (x = 2) 281 (M^+ – H, 23), 267 (M^+ – CH_3, 70), 201 (M^+ – HMe_2SiO, 80), 193 ($HMe_2SiOSiMe_2OSiMe_2H$ – Me, 87); (x = 3) 341 (M^+ – CH_3, 65), 281 (M^+ – HMe_2SiO, 80), 267 (x = 2, M^+ – CH_3, 95); (x = 4) 415 (M^+ – CH_3, 10), 355 (M^+ – HMe_2SiO, 30), 341 (40), 281 (M^+ – $HMe_2SiOSiMe_2H$, CH_3, 100), 267 (x = 2, M^+ – CH_3, 80); (x = 5) 429 (M^+ – HMe_2SiO, 5), 355 (25), 341 (25), 281 (25), 267 (25), 207 (100); (x = 6) 503 (M^+ – HMe_2SiO, 3), 429 (10), 415 (10), 355 (15), 341 (18), 281 (50), 207 (100).

Oxygen Labeling. The reaction solution from $HMe_2SiOSiMe_2H$ + $PtCl_4$ above was placed in a Schlenk tube equipped with a magnetic stir bar and connected to a vacuum manifold. The solution was subjected to three freeze/thaw/degas cycles and then opened to an atmosphere which contained 140 mm $^{18}O_2$, $^{16}O_2$, and 500 mm Ar. The solution was stirred at ambient temperature for 1 day. The gases were vented into the mass spectrometer and analyzed. In a separate experiment, a Schlenk tube containing a solid addition tube was connected to the vacuum manifold. In the solid addition tube was placed $PtCl_4$ (0.05 g, 0.15 mmol) and $HMe_2SiOSiMe_2H$ (2.5 mL, 14.5 mmol) at the bottom of the tube equipped with a magnetic stir bar. The tube was pressurized with 58 mm $^{18}O_2$, 110 mm $^{16}O_2$, and 200 mm Ar. The addition tube was tipped in such a way as to slowly add the solid $PtCl_4$. Gas evolution and yellow color formation were noted as above. The gases from this reaction were analyzed by mass spectroscopy as well. The $Pt_{colloid}$ solution prepared in ambient atmosphere and the one where it was stirred under $^{18}O_2/^{16}O_2$ were evaporated on glass slides and analyzed by Raman spectroscopy which showed a new peak at 548 cm^{-1} whose origin is unknown.

Reactions with Allylsilanes. Allyltrimethylsilane + $(EtO)_3SiH$. Allyltrimethylsilane (2 mL, 12.6 mmol) and $(EtO)_3SiH$ were combined in a glass vial, and then Karstedt's platinum catalyst was added (8 μL). Analysis by GC showed complete conversion to the expected addition product

$$(CH_3CH_2O)_3Si(CH_2)(CH_2)(CH_2)SiMe_3$$

a b c d e f

while no evidence for allylic rearranged products was found: GCMS m/e 263 (M^+ – CH_3, 40), 235 (M^+ – CH_3, CH_2CH_2, 25), 219 (40), 207 (60), 189 (90), 163 (100). ^{13}C NMR –2.51 (f), 1463 (c), 17.20 (e), 20.61 (d), 17.97 (a), 57.89 (b); ^{29}Si NMR + 0.66 (Me_3*Si*), –45.39 ($(EtO)_3$*Si*).

Et_3SiH + $H_2C{=}CHCH_2Si(OMe)_3$ (eq 4). Et_3SiH (1.89 mL, 11.9 mmol) and $H_2C{=}CHCH_2Si(OMe)_3$ (2 mL, 11.9 mmol) were combined in a glass vial, and then Karstedt's platinum catalyst (8 μL) was added. The solution was monitored by GC for 17 h (at ambient temperature) and then the solution was heated for 5 min at 130 °C. The GC analysis showed the growth of a peak at slightly higher retention time (t_R in min) for $H_2C{=}CHCH_2Si(MeO)_3$ at 1.32, new peak at 1.6, as well as peaks at higher retention times consistent with addition products (retention times of 6.8 and 7): GCMS t_R 1.32 assigned ($H_2C{=}CHCH_2Si(MeO)_3$) 162 (M^+, 20). 130 (M^+ + H – OMe, 90%), 121 (M^+ – C_3H_5, 100); t_R 1.6 assigned to $(CH_3CH_2)SiCH_2CH{=}CH_2$ 156 (M^+, 2), 127 (M^+ – Et, 70), 99 (M^+ + H–Et_2 100); t_R 6.8 assigned to $(CH_3CH_2)_3Si[CH_2]_3Si(OMe)_3$ 249 (M^+ – Et, 100), 203 (M^+ – Et, MeO, Me, 40), 175 (50), 115 (80), 117 (80); t_R 7 assigned to $(CH_3CH_2)_3Si[CH_2]_3Si(CH_2CH_3)_3$ 243 (M^+ – Et, 10), 127 (Et_3SiC^+, 40), 115 (Et_3Si^+, 100).

Et_3SiH + $H_2C{=}CHCH_2SiMe_3$ (eq 5). Et_3SiH (10 mL, 62.9 mmol) and $H_2C{=}CHCH_2SiMe_3$ were combined in a 50-mL round-bottom flask equipped with a stir bar and reflux condenser. The Karstedt's platinum catalyst (30 μL) was added, and then the solution was heated to reflux with stirring. ^{1}H NMR of

$$H_2C{=}CHCH_2SiMe_3$$

a b c d

6.41 (m, b), 5.46 (d of m, a), 2.04 (d, 8 Hz, c), 0.68 (s, d); (reaction solution) 6.3 (m, new peak), 5.46 (very weak), 2.42 (d), 1.62 (m), 0.69 (s), 0.62 (s). GCMS assigned to $Me_3Si[CH_2]_3SiMe_3$ (**4**) from reaction of $H_2C{=}CHCH_2SiMe_3$ with $HSiMe_3$) 188 (M^+, 10), 173 (M^+ – CH_3, 100), 127 (M^+ + H – $(CH_3)_4$, 100), 114 ($Me_3SiC_3H_5^+$, 60), 100 (100), 99 (100); (expected addition product $(CH_3)_3Si[CH_2]_3Si(CH_2CH_3)_3$ (**3**)) 230 (M^+, 2), 215 (M^+ – CH_3, 15), 202 (100), 201 (M^+ – Et, 100), 127 (90), 115 (100) 113 (100); (addition product $(CH_3CH_2)_3Si[CH_2]_3Si(CH_2CH_3)_3$, **5**) from the reaction of Et_3SiH with $H_2C{=}CHCH_2SiEt_3$) 243 (M^+ – Et, 100), 213 (M^+ – Et_2, H, 2), 185 (M^+ – Et_3, 3), 127 (100), 115 (100).

The products **3**, **4**, and **5** were isolated by distillation. Product **4**:

$$(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_3$$

a b c

bp 126 °C (760 mm); ^{1}H NMR 0.01 (s, a), 0.59 (t, 8 Hz, b), 0.96 (t, 8 Hz, c); ^{13}C NMR –1.54 (a), 3.56 (b), 21.32 (c); HRMS 188.1402 (M^+) calcd $C_9H_{24}Si_2$ 188.1417, found 188.1402. Note that in the fraction collected by distillation which contained **4**, an impurity was present whose ^{1}H and ^{13}C NMR spectra were consistent with

$$(CH_3CH_2)_3SiCH_2CH{=}CH_2$$

a b c d e

^{1}H NMR 0.55 (m, b), 0.98 (t, 8 Hz, a), 1.85 (d of d, 5 Hz, 2 Hz, c), 5.64 (m) and 6.1 (m) d,e; ^{13}C NMR 3.10 (b), 7.35 (a), 18.46 (c), 112.49 (e), 127.55 (d). Product **3**

$$(CH_3CH_2)_3SiCH_2CH_2CH_2Si(CH_3)_3$$

a b c d e f

bp 46–48 °C (0.15 mm); ^{1}H NMR 0.02 (s, f), 0.54 (q, 8 Hz, b), 5 lines 0.59, 0.61, 0.62, 0.64, 0.65 (*c–e*), 0.97 (t, 8 Hz, a); ^{13}C NMR –1.52 (f), 3.43 (b), 7.50 (a), 16.15 (c), 18.45 (d), 21.69 (e); HRMS 201.1502 (M^+ – Et) calcd for $C_{10}H_{25}Si_2$ 201.1495, found 201.1502. Product **5**

$$(CH_3CH_2)_3SiCH_2CH_2CH_2Si(CH_2CH_3)_3$$

a b c d

bp 82 °C (0.2 mm); ^{1}H NMR 0.51 (q, 8 Hz, b), 3 line 0.57, 0.60, 0.63 (c, d), 0.94 (t, 8 Hz, *a*); ^{13}C NMR 3.41 (b), 7.49 (a), 16.54 (c), 18.41 (d); HRMS 243.1984 (M^+ – Et) calcd for $C_{13}H_{31}Si_2$ 243.1964, found 243.1984.

Foam Reaction. The silicone foam was described by Modic.[22a] A base foam material was prepared which contained linear vinyl stopped dimethyl silicone polymers, $[Me_2(vinyl)SiO_{0.5}][Me_2SiO]_x[Me_2Si(vinyl)O_{0.5}]$, 18 g of a copolymer[30] which contains 1.4:0.25:1.0 $[Me_3SiO_{0.5}]/[Me(vinyl)SiO]/SiO_2$; 24.7 g of alpha quartz, and 58 μL of Karstedt's platinum catalyst. Combining 20 g of the base formulation with 0.3 g of H_2O and 1.33 g of a linear methyl stopped methyl hydrogen polymer, $[Me_3SiO_{0.5}][Me(H)SiO]_x[Me_3SiO_{0.5}]$, average x = 25, and hand mixing for 30 s gave a foamed and crosslinked material with release of H_2. The experiment was repeated except that first D_2O was used in place of H_2O and the foam was made in a glass apparatus that could be quickly sealed after mixing so that the gases could be collected. Analysis of the gases from the reaction showed 1.7:1.0 H_2/HD (repeat 1.6:1.0) and D_2 was not observed. Analysis of the foam made with H_2O by ^{1}H NMR showed the following resonances: 5.77 (vinyl), 4.5 (SiH), and 2.7 (H_2O). Analysis of the foam made with D_2O by ^{2}D NMR showed the following resonances: 6.25 (vinyl), 4.89 (SiD), and 3.17 (D_2O); peaks due to hydrogenated products were not observed.

Acknowledgment. Dr. Rob Colborn (GE CRD) and Dr. Rich Uriarte (GE Silicones) participated in many helpful discussions. Dr. Arnold Factor assisted in the oxygen labeling experiment. Dr.

---

(30) Daudt, W. H.; Tyler, L. J. U.S. patent 2,676,182, 1954.

Ken Smith is acknowledged for his wonderful efforts in setting up the NMR. Dr. Elizabeth Williams and Ms. Joanne Smith ran the ^{29}Si NMRs, Ralph May, Steve Dorn, and Hans Grade carried out the mass spectrometry analyses, and Dr. Pete Codella carried out the Raman measurements. Professor Sam Danishefsky, Yale University, is thanked for suggesting the allyltrimethylsilane experiments. Cindy Herderich is thanked for help in preparing this manuscript.

Supplementary Material Available: Figure showing relative rate of addition of $(EtO)_3SiH$ to $Me_3Si(vinyl)$ and styrene (1 page). Ordering information is given on any current masthead page.

Photochemistry of Triarylsulfonium Salts

John L. Dektar and Nigel P. Hacker*

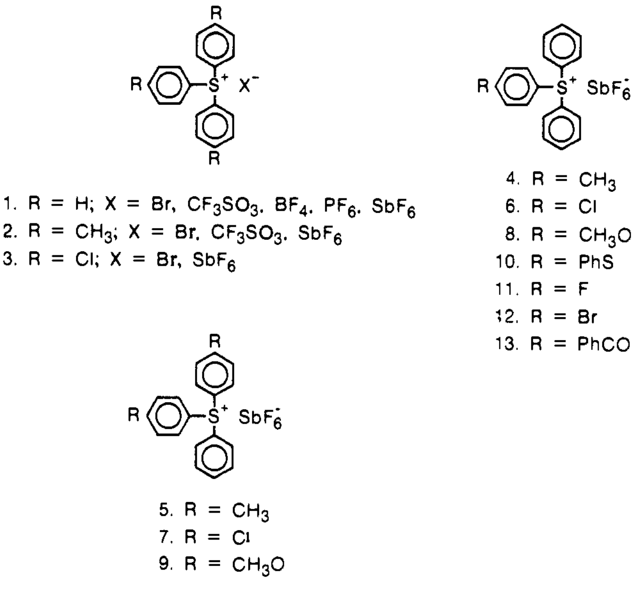
Contribution from the IBM Research Division, Almaden Research Center, San Jose, California 95120-6099. *Received August 11, 1989*

Abstract: The photolysis of triphenylsulfonium, tris(4-methylphenyl)sulfonium, tris(4-chlorophenyl)sulfonium, several monosubstituted (4-F, 4-Cl, 4-Me, 4-MeO, 4-PhS, and 4-PhCO), and disubstituted (4,4′-Me_2 and 4,4′-$(MeO)_2$) triphenylsulfonium salts was examined in solution. It was found that direct irradiation of triphenylsulfonium salts produced new rearrangement products, phenylthiobiphenyls, along with diphenyl sulfide, which had been previously reported. Similarly, the triarylsulfonium salts, with the exception of the [4-(phenylthio)phenyl]diphenylsulfonium salts, gave the new rearrangement products. The mechanism for direct photolysis is proposed to occur from the singlet excited state to give a predominant heterolytic cleavage along with some homolytic cleavage. The heterolytic cleavage gives phenyl cation and diphenyl sulfide, whereas homolytic cleavage gives the singlet phenyl radical and diphenylsulfinyl radical cation pair. These pairs of intermediates then produce the observed photoproducts by an in-cage recombination mechanism and also by reactions with the solvent. The effect of solvent viscosity, solvent polarity, anion, and aryl substituent was examined. The triplet sensitization of the sulfonium salts was also investigated. In contrast to previous reports, the triplet state of the sulfonium salt is labile, leading to a triplet geminate radical pair of phenyl radical and diphenylsulfinyl radical cation. These species ultimately form benzene and diphenyl sulfide as products. Direct photolysis of the [4-(phenylthio)phenyl]diphenylsulfonium salt, gave exclusively diphenyl sulfide, benzene, and acid and decomposes via the triplet excited state.

Introduction

Triarylsulfonium salts have found importance in industry as photoinitiators for cationic polymerization and as "photoacid" generators.[1,2] Sulfonium salt photochemistry is also of basic interest due to the variety of intermediates formed, and this has resulted in several studies of the photochemistry of these salts.[3-13] These studies suggest that the reaction originates from the excited singlet state of the triarylsulfonium salt and that a phenyl moiety fragments from the triarylsulfonium salt by either a homolytic pathway, to give either a phenyl radical and a diphenylsulfinyl

Chart I



1. R = H; X = Br, CF_3SO_3, BF_4, PF_6, SbF_6
2. R = CH_3; X = Br, CF_3SO_3, SbF_6
3. R = Cl; X = Br, SbF_6

4. R = CH_3
6. R = Cl
8. R = CH_3O
10. R = PhS
11. R = F
12. R = Br
13. R = PhCO

5. R = CH_3
7. R = Cl
9. R = CH_3O

---

[1] (a) Crivello, J. V. *UV Curing: Science and Technology*; Pappas, S. P., Ed.; Technology Marketing Corporation: Stanford, CT, 1978; p 23. (b) Crivello, J. V. *CHEMTECH* **1980**, *10*, 624. (c) Pappas, S. P. *Radiat. Curing* **1981**, *8*, 28. (d) Crivello, J. V. *Polym. Eng. Sci.* **1983**, *23*, 953. (e) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1. (f) Pappas, S. P. *Prog. Org. Coat.* **1985**, *13*, 35. (g) Pappas, S. P. *J. Imaging Technology* **1985**, *11*, 146. (h) Crivello, J. V. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 145. (i) Yagci, Y.; Schnabel, W. R. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 161. (j) Willson, C. G.; Bowden, M. J. *CHEMTECH* **1989**, *19*, 182.

[2] (a) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012. (b) Ito, H.; Willson, C. G. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series 242 American Chemical Society: Washington, DC, 1984; p 11.

[3] (a) Knapzyck, J. W.; McEwen, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 145. (b) Knapzyck, J. W.; McEwen, W. E. *J. Org. Chem.* **1970**, *35*, 2539. (c) Knapzyck, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* **1971**, 3739.

[4] Davidson, R. S.; Goodin, J. W. *Eur. Polym. J.* **1982**, *18*, 589.

[5] Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.

[6] Crivello, J. V.; Lee, J. L.; Conlon, D. A. *J. Radiat. Curing* **1983**, 6.

[7] Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* **1979**, *23*, 140.

[8] Pappas, S. P.; Gatechair, L. R.; Pappas, B. C. *J. Photochem.* **1981**, *17*, 120.

[9] Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Schnabel, W. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 69.

[10] Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77.

[11] Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Jilek, J. H.; Schnabel, W. *Polym. Photochem.* **1984**, *5*, 1.

[12] Gatechair, L. R. Ph.D. Dissertation, North Dakota State University, 1981.

[13] Pappas, S. P.; Gatechair, L. R. *Proc. Water-borne Higher-Solids Coat. Symp. 8th* **1981**, *8*, 85.

0002-7863/90/1512-6004$02.50/0