Journal of Organometallic Chemistry, 352 (1988) 81–94
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Silane-silanol dehydrocondensation. The microscopic reverse of hydrogen activation by an organometallic oxide complex *

R.J. Klingler, T.R. Krause, and J.W. Rathke

Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, Illinois 60439 (U.S.A.)

(Received December 1st, 1987)

Abstract

Hydrogen evolution from the dehydrocondensation reaction of triphenylsilane with triphenylsilanol is catalyzed by sodium trimethylsiloxide at 90 ° C in dioxane solvent. This system is the first example of a silane hydrolysis reaction that exhibits simple first order kinetics when investigated under second order conditions, equal concentrations of silane to proton source. Further analysis of the kinetics by the method of initial rates indicates that the reaction is first order in silane and zero order in silanol, demonstrating a multistep mechanistic process and that the proton source is not involved in the rate limiting step. The microscopic reverse process, hydrogen activation, has been investigated at 200–250 ° C and 330 atm of hydrogen using hexamethyldisiloxane and sodium trimethylsiloxide to yield significant, 12%, quantities of trimethylsilyl hydride; however, the reaction has limited application since the methyl groups are concurrently cleaved to the organic product methane under these conditions.

Introduction

Recently we have been intrigued by the concept of using simple organosiloxane complexes as soluble metal oxide methanol synthesis catalysts [1]. Previous work [2] has centered on defining those steps which directly result in the production of the organic product methanol: ketonic decarboxylation of formate, Tischenko dimerization of formaldehyde, and the decarbonylation of methyl formate as given in eqs. 1–3, respectively.

$$2Me_3SiO_2CH \rightarrow CH_2{=}O + CO_2 + Me_6Si_2O \qquad (1)$$

$$2CH_2{=}O \rightarrow HCO_2CH_3 \qquad (2)$$

$$HCO_2CH_3 \rightarrow CH_3OH + CO \qquad (3)$$

---

* Work supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under contract W-31-109-ENG-38.

0022-328X/88/$03.50

Furthermore, the required formate reactant for the net disproportionation process of eqs. 1–3 is available both through the carbonylation of hydroxide [1], eq. 4 and

$$Me_3SiOH + CO \rightarrow Me_3SiO_2CH \qquad (4)$$

the carboxylation of hydride [1,3], eq. 5.

$$Me_3SiH + CO_2 \rightarrow Me_3SiO_2CH \qquad (5)$$

Therefore, the hydrogen activation process indicated in eq. 6 would complete a

$$Me_6Si_2O + H_2 \rightarrow Me_3SiOH + Me_3SiH \qquad (6)$$

closed catalytic cycle for methanol synthesis from carbon monoxide and hydrogen, eq. 7, since the process in eq. 7 results as the sum of twice eqs. 1, 4, 5, and 6, plus

$$CO + 2H_2 \rightarrow CH_3OH \qquad (7)$$

eqs. 2 and 3. Furthermore, while the formate chemistry in eqs. 1–5 is rapid at 250 °C, the steady state rate of methanol synthesis using hexamethyldisiloxane is slow, even at 300 °C and 310 atm of synthesis gas [1]. These observations suggest that the hydrogen activation process in eq. 6 is rate limiting under these conditions and has caused our attention to become focused more closely on this very elementary reaction process for an organometallic oxide moiety. Significantly, the microscopic reverse step for an analogous reaction, silane alcoholysis in eq. 8, has been

$$R_3SiH + R'OH \rightarrow R_3SiOR' + H_2 \qquad (8)$$

extensively investigated as documented in a recent review [4]. Similar to the hydrogen activation process in eq. 6, the uncatalyzed silane alcoholysis of eq. 8 is also quite slow. The addition of a small quantity of a base catalyst, however, has a pronounced effect on the latter process. A variety of organic and inorganic bases have now been reported with alkali metal alkoxides being the most effective and, therefore, widely studied catalysts for silane hydrolysis. We report here the dehydrocondensation reaction of triphenylsilane with triphenylsilanol, eq. 9, catalyzed by

$$Ph_3SiH + Ph_3SiOH \xrightarrow[90\,^\circ C]{NaOSiPh_3} Ph_6Si_2O + H_2 \qquad (9)$$

sodium triphenylsiloxide in dioxane solution at 90 °C. In contrast to the alcoholysis reaction of eq. 8, the kinetics of the silanol system, eq. 9, are independent of the concentration of the proton source and as such provides a useful mechanistic compliment to the careful kinetic isotope effect studies which have been reported on the silane alcoholysis reaction.

Results

Previous work on methanol synthesis with organosiloxane complexes has employed primarily trimethylsilyl derivatives due to their high hydrocarbon solubility and favorable reaction rates for formate disproportionation in eqs. 1–3. Thus, the disproportionation of trimethylsilyl formate to methyl formate, carbon dioxide, and hexamethyldisiloxane exhibits net first order reaction kinetics with a half life of 7 h^{-1} at 250 °C in dioxane solution [2]. However, under the same conditions the corresponding triphenylsilyl formate derivative is slower exhibiting a somewhat longer half life of 22 h^{-1}. In contrast, the phenyl derivatives are the substrate of

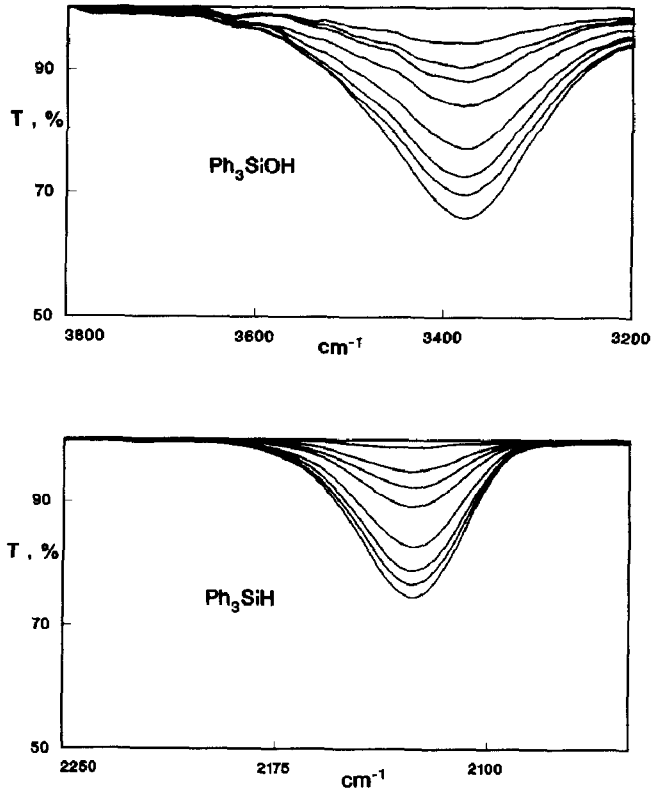


Fig. 1. Infrared transmission bands at selected time intervals during the reaction of triphenylsilanol with triphenylsilane in dioxane with sodium triphenylsiloxide catalyst at 90 ° C.

choice for investigating the dehydrocondensation reaction of eq. 9 since triphenylsilanol is more stable than trimethylsilanol towards concurrent dehydration, eq. 10.

$$2Ph_3SiOH \rightarrow Ph_6Si_2O + H_2O \qquad (10)$$

The latter reaction is a process which potentially complicates the kinetics of the dehydrocondensation reaction of eq. 9 by providing an alternative pathway for consumption of the silanol reactant. In addition, the majority of the comparative work on silane alcoholysis in eq. 8 has employed triarylsilanes.

The reaction between triphenylsilane and triphenylsilanol was conveniently followed spectrophotometrically, FTIR, by measuring the decrease in the absorbances of the silicon hydride stretch and the silicon hydroxyl stretch at 2125 and 3374 cm^{-1}, respectively, in Fig. 1. It is noted that the silicon hydroxyl stretching frequency is cleanly resolvable from that due to water which may be independently quantitated at 3505 cm^{-1}. The triphenylsilane and triphenylsilanol concentrations were observed to decrease in the anticipated one-to-one ratio, left side of Fig. 2, concurrent with the generation of one equivalent of dihydrogen in the gas phase, right side of Fig. 2, as required by the stoichiometry of eq. 9 when the reaction was conducted under simple second order conditions; i.e., using equal concentrations of silane and silanol. Furthermore, under these second order conditions it was observed to exhibit net first order kinetics, as demonstrated in Fig. 3 at three sodium triphenylsiloxide catalyst concentrations. First order rate plots in triphenylsilane

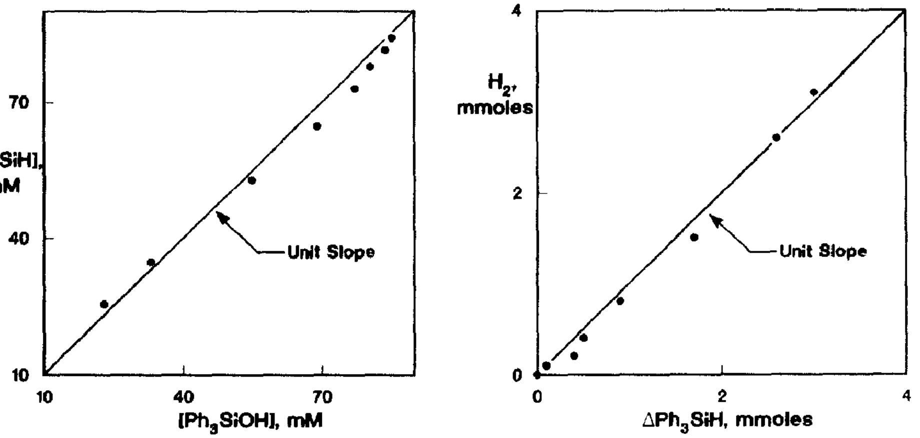


Fig. 2. Stoichiometric analysis of silane-silanol dehydrocondensation at 90 °C with triphenylsilane, 85.1 m*M*, triphenylsilanol, 84.0 m*M*, and sodium triphenylsiloxide, 84 m*M*, in dioxane solvent.

concentration were linear for over three half-lives. Alternatively, if the dehydrocondensation reaction is conducted under pseudo first order conditions of excess proton source, triphenylsilanol, the system becomes complicated by the silanol's concurrent dehydration, eq. 10, leading to the production of water, column 4 in Table 1, at extended reaction times. For this reason, all kinetic rate constant measurements were obtained by initial first order rate analysis on the triphenylsilane concentration over a time period where the water concentration was confirmed by FTIR to be small. It is further noted that even in the presence of the silanol dehydration reaction in eq. 10, the total proton concentration, for example column 5 in Table 1,

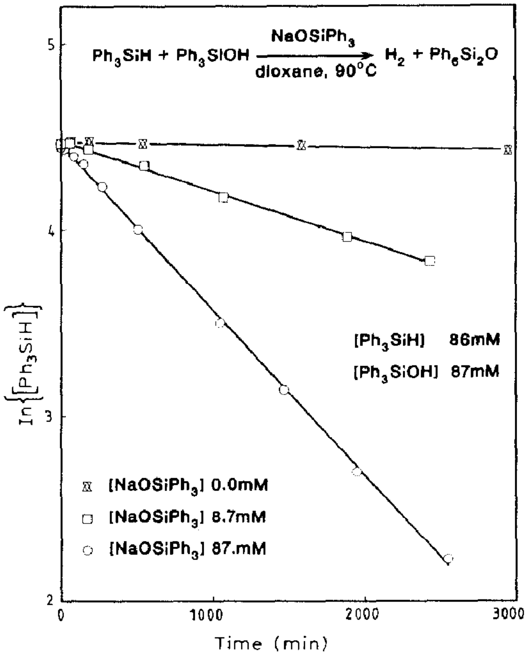


Fig. 3. First order rate plots for silane-silanol dehydrocondensation.

Table 1

Proton balance for silane hydrolysis with concurrent silanol dehydration [a]

Time (min)	$[Ph_3SiH]$ (m*M*)	$[Ph_3SiOH]$ (m*M*)	$[H_2O]$ (m*M*)	$[H^+]_T$ (m*M*)	$[H^+]_T + \Delta SiH$ [b] (m*M*)
0	82	230	0	230	230
30	80	219	6	231	233
60	76	205	9	223	229
90	72	195	14	223	233
120	68	185	15	215	229
150	64	176	15	206	224
600	17	100	36	172	237
1145	0.1	53	51	155	237

[a] At 90 °C in dioxane solution with $[NaOSiPh_3]$ 84 m*M*. [b] Sum of the total proton concentration plus the net change in the triphenylsilane concentration.

is seen to decay in accord with the consumption of the hydride, column 2, as evident by the consistency of the total proton balance given in the last column of Table 1.

Discussion

The hydrolytic cleavage of a silicon hydride moiety with the proton from an organosilanol is an example of the more general alcoholysis reaction in eq. 8 from a stoichiometric consideration. However, the particular case in eq. 9 is important since it corresponds to the microscopic reverse direction of the reaction for the activation of hydrogen by an organometallic oxide complex. Furthermore, as will be presently discussed, the silanol system in eq. 9 exhibits kinetic behavior different than that which has been reported for the analogous hydrolysis with alcohols, eq. 8. Therefore, it is possible that they proceed by different mechanisms. Furthermore, since the dehydrocondensation reaction in eq. 9 is best understood within the context of the more general case, the discussion begins with a presentation of the salient features of the latter process.

Mechanism of silane alcoholysis

Previous discussions of the mechanism for silane alcoholysis, eq. 8, have considered the three possibilities embodied by a concerted trimolecular process, a pentacoordinate silane intermediate, and a free alkali metal hydride containing pathway given in eqs. 11–15, respectively [4]. Unfortunately, distinguishing between these possibilities is difficult since the rate law is complex exhibiting kinetic orders in each of the reactants, hydride and proton source, as well as the base catalyst. However,

Concerted

$$R'O^- + R_3SiH + R''OH \rightarrow R_3SiOR' + H_2 + R''O^- \quad (11)$$

Pentacoordinate silane

$$R'O^- + R_3SiH \rightarrow (R'O)R_3SiH^- \quad (12)$$

$$(R'O)R_3SiH^- + R''OH \rightarrow R_3SiOR' + H_2 + R''O^- \quad (13)$$

Free hydride

$$R'O^- + R_3SiH \rightarrow R_3SiOR' + H^- \quad (14)$$

$$H^- + R''OH \rightarrow R''O^- + H_2 \quad (15)$$

since the reported rate law for silane alcoholysis does contain a kinetic order in the proton source, the reactions in eqs. 12 and 14 (if they occur at all) must exhibit some degree of reversibility, since the proton source does not appear until eqs. 13 and 15, respectively. This conclusion was nicely corroborated by a detailed analysis of the solvent isotope effect [5] interpreted in terms of hydrogen bonding by the alcoholic solvent to the lone pairs of the alkoxide catalyst which indicated that no net consumption of alkoxide ion occurs within the rate limiting step plus any prior equilibrium (it is noted that the solvent isotope effect is not to be confused with the primary isotope effects for deuterium labeling at either the hydride or the proton centers, which have also been reported) [4]. Further conclusions are also dependent on isotope effects. Thus, if one assumes that the reaction in eq. 15 is diffusion controlled, it is possible to rule out the free hydride mechanism [6] in eqs. 14, 15 on the basis of the large product isotope preference observable upon partial deuteration at the proton source. Lastly, arguments against the concerted process [6,7], eq. 11, have been proposed in light of the Hammond postulate with respect to alkyl substitution at the silicon hydride center. Therefore, cumulative investigations favor the pentacoordinate silane mechanism [4], with the reaction in eq. 12 established as a rapid equilibrium prior to the rate limiting step in eq. 13. Indeed, anionic pentacoordinate silicon hydrides analogous to the proposed intermediate have subsequently been reported in the gas phase [8] and structurally characterized anionic pentacoordinate silicon alkyl complexes have been known for some time [9]. Hypercoordinate silatranes such as $HSi(OCH_2CH_2)_3N$ which contain an intramolecular N → Si dative bond are known to exhibit unusually low Si–H stretching frequencies and high chemical reactivities [10], in addition, a pentacoordinate silicon hydride intermediate analogous to that in eq. 12 has been proposed in the reduction of aldehydes and ketones to the corresponding alcohols [11].

Mechanism of silane-silanol dehydrocondensation

A direct consequence of the pentacoordinate silane mechanism of eqs. 12, 13 is that as one goes to less basic catalysts or more acidic proton sources, eventually a point should be reached where the reaction in eq. 13 becomes faster than the reverse of the process in eq. 12. Under those conditions eq. 12 is effectively irreversible in the forward direction, and the kinetics of the system will be independent of the concentration of the proton source. Indeed, the dehydrocondensation reaction in eq. 9 (which employs the less basic triphenylsiloxide catalyst in comparison to the methoxide catalyst of eq. 8) is not first order in both the proton source and the hydride source, since the system exhibits simple first order kinetics, Fig. 3, for over three half-lives when conducted under second order conditions, equal concentrations of silane to silanol. This observation immediately rules out a concerted trimolecular reaction, such as that in eq. 11. Specific experiments designed to directly determine the kinetic order in triphenylsilanol were complicated, however, by its concurrent dehydration, eq. 10, at higher concentrations (dehydrations can be second order in alcohol) [12]. Furthermore, the apparent reaction rate constant was seen to increase in those experiments at high silanol concentration where water was produced as demonstrated in Fig. 4 by plotting the effective (average pairwise) first order rate constant vs. the average water concentration for the data in Table 1. Significantly, the nonzero intercept in Fig. 4 demonstrates residual triphenylsilanol reactivity for silane hydrolysis at low water content. The initial rate constant data

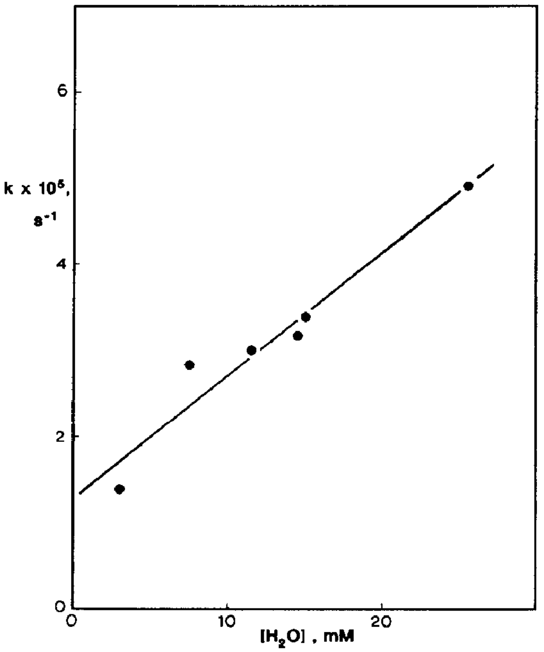


Fig. 4. Dependence of the first order rate constant for silane decay in triphenylsilane-triphenylsilanol dehydrocondensation on the water concentration at 90 °C in dioxane.

for triphenylsilane decay is presented in column 3 of Table 2 and is seen to be independent of the triphenylsilanol concentration consistent with the pentacoordinate silane intermediate mechanism, eqs. 12, 13, with rate limiting triphenylsiloxide base addition, eq. 12 with R = Ph and R′ = $SiPh_3$. The accelerating effect of water, Fig. 4, may be due to hydrolysis of the silane with the more acidic proton source in eq. 16 vs. the triphenylsilanol in eq. 9. However, that would be inconsistent with the

$$Ph_3SiH + H_2O \rightarrow Ph_3SiOH + H_2 \qquad (16)$$

assignment of triphenylsiloxide addition, eq. 12, as the effectively irreversible rate limiting step. Alternatively, since the reactions were conducted in the nonpolar organic solvent dioxane, it is possible that the water solvates the sodium triphenyl-

Table 2

Initial rate constant for silane hydrolysis at various concentrations for the proton source [a]

$[Ph_3SiH]_i$ (mM)	$[Ph_3SiOh]_i$ (mM)	Initial rate	
		k [b] ($\times 10^5$ s^{-1})	Conversion [c] (%)
85	7	1.0 (0.1)	8
86	47	1.3 (0.1)	17
85	84	1.5 (0.2)	98
86	165	1.4 (0.4)	8
82	230	1.7 (0.5)	3

[a] At 90 °C in dioxane solution with $[NaOSiPh_3]$ = 85 mM. [b] Error limits given in parentheses. [c] Listed percent conversion is based on silane even in those experiments where the silanol was the limiting reagent.

siloxide catalyst converting it to a stronger base by breaking up ionic aggregates. The structure of the sodium triphenylsiloxide catalyst in dioxane solvent is not known. However, potassium trimethylsiloxide in both the solid and vapor state exists as a discrete tetramer, while the solid state structure consists of potassium and trimethylsiloxide ions occupying alternating apices of a cubic cluster [13]. Furthermore, this entire question of discrete ionic clusters raises yet another mechanistic possibility for the dehydrocondensation reaction of eq. 9. The proposed mechanism in eqs. 17, 18 employs discrete cubic clusters based on potassium trimethylsiloxide as a model complex; however, the exact molecularity is not an essential feature of the scheme.

Hydride cluster

$$Ph_3SiH + [NaOSiPh_3]_4 \rightarrow Ph_6Si_2O + NaH \cdot [NaOSiPh_3]_3 \qquad (17)$$

$$NaH \cdot [NaOSiPh_3]_3 + Ph_3SiOH \rightarrow [NaOSiPh_3]_4 + H_2 \qquad (18)$$

The hydride cluster mechanism of eqs. 17, 18 differs from the free hydride mechanism of eqs. 14, 15 in that it is no longer possible to be confident that the rate of protic cleavage, eq. 18, will be near the diffusion limit, compare eq. 15. Fortunately, eqs. 12, 13 and eqs. 17, 18 are fundamentally similar in that free sodium hydride is not produced, rather it is carried complexed to a Lewis acid inherent to the system. The mechanistic possibility of eqs. 17, 18 has been included to recognize that the organosilicon moiety is not the only Lewis acid present in the alkali metal siloxide catalyzed dehydrocondensation reaction in eq. 9. Both eqs. 12, 13 and eqs. 17, 18 are consistent with the observed kinetics.

Nucleophilic hydrogen activation

Hydrogen evolution from the condensation reaction of triphenylsilane with triphenylsilanol, eq. 9, is strongly catalyzed by the addition of millimolar quantities of sodium triphenylsiloxide, as demonstrated in Fig. 3. Therefore, based on the principle of microscopic reversibility [14], simple Lewis base substrates, such as sodium triphenylsiloxide, will catalyze the hydrogenation of the corresponding organosiloxane complex. Though mechanistically formal, this statement may have limited practical application for the siloxane catalyzed methanol synthesis system of eqs. 1–7. Thus, even with no kinetic barrier, the process in eq. 6 is thermodynamically [15] uphill by nearly 20 kcals. Therefore, if alternative degradative pathways exhibit activation barriers smaller than the above 20 kcal limit, then the siloxane hydrogenation in eq. 6 would be dominated by the more facile production of these alternative decomposition products. The reaction of hexamethyldisiloxane under 330 atm of hydrogen with a sodium trimethylsiloxide catalyst was conducted in a variety of solvents as summarized in column 3 of Table 3. Two conclusions were apparent upon completing this series of experiments. First, the overall level of reactivity was dramatically increased in the presence of the basic sodium trimethylsiloxide additive, as indicated by comparison of the silane produced, column 7, in rows 1 and 2 of Table 3. Second, significant quantities of trimethylsilyl hydride, column 7 in Table 3, were produced in relation to the initial charge of hexamethyldisiloxane, as indicated in the last column of Table 3. It is noted that trimethylsilyl hydride was not produced in the control experiments conducted under

Table 3

Summary of nucleophilic hydrogen activation reactions [a]

$[(CH_3)_6Si_2O]$ (M)	$[NaOSi(CH_3)_3]$ (M)	Solvent	Gas [b] phase	Reaction temp (°C)	CH_4 (mmoles)	$(CH_3)_3SiH$ (mmoles)	$\frac{(CH_3)_3SiH}{(CH_3)_6Si_2O}$ [c]
1	0	Dioxane	H_2	250	0.5 [d]	0.0 [e]	0.00
1	0.1	Dioxane	H_2	250	76	20	0.11
1	0.1	Dioxane	H_2	200	34	21	0.12
1	0.1	Dioxane	Ar [f]	200	12	0.0 [e]	0.00
1	0.1	Dioxane	Ar [g]	200	12	0.0 [e]	0.00
0	0.1	Dioxane	Ar [h]	200	18	0.0 [e]	[i]
4.7	0.1	$[(CH_3)_6Si_2O]$	H_2	200	45	38	0.04
0	0.1	$B[OSi(CH_3)_3]_3$	H_2	200	4	1	[i]

[a] Reactions were periodically samples over a 96 h period. [b] At 330 atm. [c] Ratio of the moles of silane produced to the initial charge of siloxane present in the 180 ml of solution phase. [d] Also produce 0.4 mmol of $(CH_3)_3SiOH$. [e] Less than the detection limit of 10 μmol. [f] Hydrogen at 0.92 atm corresponding to 3.0 mmol was produced. [g] Hydrogen at 0.80 atm corresponding to 2.6 mmol was produced. [h] Hydrogen was not observed. [i] Not applicable.

an inert gas, rows 4 through 6 in Table 3. In contrast to the stoichiometry of eq. 6, significant quantities of trimethylsilanol were not detected; and large quantities of methane, column 6 in Table 3, were produced. Base catalyzed solvolysis of hexamethyldisiloxane is documented [16] and apparently competes quite favorably with simple hydrogenation in this system. The mechanism by which methane is produced in this system is not known with certainty; however, recently Eaborn and Stanczyk have suggested that sodium trimethylsiloxide reacts to give methyl sodium [17], eq. 19, which would produce methane at 250°C with an adventitious proton source,

$$NaOSi(CH_3)_3 \rightarrow NaCH_3 + O{=}Si(CH_3)_2 \qquad (19)$$

such as the missing trimethylsilanol from eq. 6. Indeed, consistent with Eaborn's suggestion for the sodium salt, it has been reported that the thermolysis of an analogous zinc trimethylsiloxide complex gives a crystallographically identified product with a zinc methyl bond [18], eq. 20.

$$\left[Zn(OSiMe_3)_2\right]_n \rightarrow \frac{n}{4}[MeZnOSiMe_3]_4 + (Me_2SiO)_n \qquad (20)$$

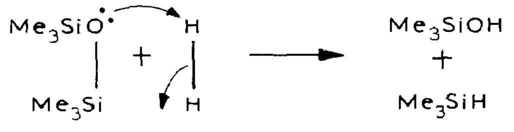
Furthermore, since a standard method of synthesizing trimethylsilanolate is from methyl lithium [19], eq. 21, it is possible that the reaction in eq. 21 is reversible at

$$(Me_2SiO)_n + n\text{LiMe} \rightarrow n\text{LiOSiMe}_3 \qquad (21)$$

250°C. An attempt was made to slow the alkyl group elimination of eq. 19 by employing an acidic solvent which could coordinate with and, hopefully, stabilize the sodium trimethylsiloxide. Comparison of the last two rows of Table 3 indicates that the rate of methane production is slower in the tris(trimethylsilyl) borate solvent than that observed in the noncoordinating analog, hexamethyldisiloxane. However, there was no improvement in the hydride to methane selectivity, since the rate of trimethylsilyl hydride formation was also correspondingly lower. Therefore, while organosiloxane compounds are well suited to cleanly demonstrate Lewis base catalysis in the thermodynamically favorable hydrogen evolution direction, eq. 9, investigation of Lewis base catalyzed hydrogen activation in the direction of interest, eq. 6, for synthesis gas transformations is complex. Thus, steady state methanol synthesis in eq. 7 is observable at 300 °C and 310 atm of synthesis gas; however, the reaction is too slow to establish catalytic turnovers, based on silicon in a reasonable time frame [1]. In contrast, the addition of sodium trimethylsiloxide to increase the overall basicity of the system has a pronounced effect on the rate of formation of the key organometallic intermediate, trimethylsilyl hydride; however, facile alkyl elimination, such as that in eq. 19, becomes a problem under these conditions. It is cautioned that this latter complication, alkyl group elimination, encountered with the highly basic trialkylorganosiloxide substrate does not imply that nucleophilic hydrogen activation is inherently slow or otherwise unimportant. Thus, aqueous sodium hydroxide catalyzes hydrogen/deuterium exchange under relatively mild conditions [20,21] and sodium butoxide has been employed as a nontransition metal hydrogenation catalyst [22]. Furthermore, the competitive alkyl group cleavage which limits the use of sodium trimethylsiloxide for homogeneous nucleophilic hydrogen activation, see column 6 in Table 3, would not be a limitation for a heterogeneous metal oxide catalyst since the latter type catalyst does not similarly depend on alkyl substituents for stability or solubility. Therefore, these results underscore the need for organometallic oxide substrate complexes with the cationic portions sufficiently tightly ligated to resist solvolytic degradation under strongly basic conditions before the field of homogeneous catalysis will ultimately emulate all the chemistry occurring on heterogeneous metal oxide catalysis in syngas transformations.

Nature of the transition state

The hydrogen activation process in eq. 6 belongs to the general stoichiometric classification of heterolytic cleavage in which the dihydrogen molecule is split into both a hydride containing and a proton containing residue [23]. The transition state for heterolytic hydrogen activation is frequently described by a four-center/four-electron activated complex in which a Lewis acid, in this case a trimethylsilyl center, and a Lewis base, in eq. 6 an oxygen centered nonbonding electron pair, assist by coordinating to the leaving hydride and proton moieties, respectively, as indicated in eq. 22. However, it is noted that the Lewis acid and Lewis base are not



(22)

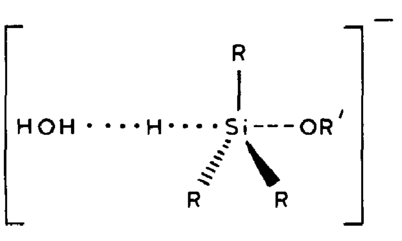
necessarily equal partners in the process. For example, there is a growing consensus that heterolytic hydrogen activation by early transition metal and organoactinide alkyl complexes proceeds by such a four-center/four-electron transition state and that the Lewis acid site at the metal center is more influential than the Lewis base site at the alkyl moiety [24]. Interestingly, one of the strongest cases for heterolytic hydrogen activation occurring predominantly at the Lewis base site also comes from the field of alkylmetal chemistry. Thus, the hydrogenation of butyllithium proceeds rapidly at room temperature even at low subatmospheric hydrogen partial pressures to yield butane and lithium hydride [25], eq. 23.

$$\mathrm{BuLi} + \mathrm{H_2} \rightarrow \mathrm{BuH} + \mathrm{LiH} \tag{23}$$

Furthermore, addition of polyamines to the butyllithium system, eq. 23, accelerates the hydrogenation process presumably by increasing the Lewis basicity of the resulting butyl moiety [25]. Significantly, continued addition of even a large excess of the polyamine ligand is reported to have no adverse effect on the rate of hydrogenation and, therefore, argues against any general requirement of highly accessible Lewis acid sites for rapid hydrogen activation. Similarly, our results as well as those of previous workers [4], indicate that the rate of hydrogen evolution/activation by organosilicon compounds in eqs. 6, 8, and 9 is strongly influenced by the addition of either organic or inorganic Lewis base catalysts. These observations suggest that the main group systems in eqs. 6 and 23 are to be considered predominantly nucleophilic in their major electronic driving force. This reactivity pattern would result if the Lewis base interacts more strongly than the relatively hard main group Lewis acid with the dihydrogen molecule in the proposed four-center/four-electron transition state. Consistent with the proposal that hydrogen may be activated by nucleophilic oxygen centers, a recent ab initio molecular orbital calculation [26] based on optimized geometries with an expanded atomic orbital basis set predicts significant not bonding interaction, up to 9.1 kcal, between dihydrogen and free hydroxide ion, even in the complete absence of coordinating metal countercations, eq. 24.

$$\mathrm{HO^-} + \mathrm{H_2} \rightleftharpoons \underset{(\mathrm{I})}{[\mathrm{HO}\ldots\mathrm{H_2}]^-} \rightleftharpoons \underset{(\mathrm{II})}{[\mathrm{HOH}\ldots\mathrm{H}]^-} \rightleftharpoons \mathrm{HOH} + \mathrm{H^-} \tag{24}$$

Surprisingly, two distinguishable energy minimum or intermediates, I and II, were calculated for the reaction in eq. 24. The promotional effect of Lewis acids was not considered in the calculation; however, coordination of the acidic silicon center of a tetravalent organosiliconalkoxide to either intermediate I or II is likely to stabilize them further as suggested below in III for such an organosilicon complex with II.



(III)

Transition states with structures similar to III have been proposed [6,7] for the rate-limiting step, eq. 13, of the pentacoordinate silane mechanism of eqs 12, 13. Interestingly, the calculation of eq. 24 suggests that the reaction of eq. 13 may be, in fact, a composite process with two distinct intermediates as indicated with the general Lewis acid, A, in eq. 25.

$$\mathrm{HO^-} + \mathrm{H_2} + \mathrm{A} \rightleftharpoons [\mathrm{HO}\ldots\mathrm{H_2}\ldots\mathrm{A}]^- \rightleftharpoons [\mathrm{HOH}\ldots\mathrm{H}\ldots\mathrm{A}]^- \rightleftharpoons \mathrm{HOH} + \mathrm{HA^-} \tag{25}$$

Lastly, it is noted that free hydride ion should not exist in condensed solution phase within these metal oxide hydrogen activation/evolution systems since the reaction of hydride ion with water in eq. 24 is calculated to proceed to intermediate II with no activation barrier [26]. Indeed, analysis of the experimental product isotope distribution has previously ruled out a free hydride intermediate [6] in the silane alcoholysis reaction of eq. 8.

Conclusions

Notably, both the silane-silanol dehydrocondensation reaction, eq. 9, and the more general silane hydrolysis reaction, eq. 8, are catalyzed by Lewis base complexes with the implication that the microscopic reverse hydrogen activation by at least this class of organometallic oxo complex proceeds through a mechanistic pathway which is inherently different from those which are usually encountered with transition metal hydrogenation catalysts [27]. Thus, within the field of transition metal catalysis, a heavy emphasis is traditionally placed on the role of Lewis acid sites at the metal center and general oxidative addition/reductive elimination pathways [28,29]. Alternatively, the rate of heterolytic hydrogen evolution/activation with main group organosilicon oxo complexes depends primarily on the strength of the Lewis base site located on the oxide moiety and proceeds with no formal change in oxidation state. Therefore, this alternative class of oxide dominated heterolytic hydrogen activation is open to high oxidation state silicon IV siloxides and may find general application with other high oxidation state metal oxide complexes with similarly hard Lewis acid site(s) at their respective metal centers.

Experimental

Materials

Triphenylsilane, triphenylsilanol, hexamethyldisiloxane, hexamethyldisilane, trimethyl borate, and 1,4-dioxane were purchased from Aldrich Chemical Company and trimethylsilane from Petrarch Systems. The sodium trialkylsiloxides were prepared from the corresponding silanol and excess sodium metal in diethyl ether using a standard procedure [30]. Unreacted sodium was removed by filtration under argon and the ether solvent was removed in vacuo at room temperature. The solid sodium trimethylsiloxide thus obtained was readily soluble in pentane solution indicative of low residual hydroxyl content, which would be evident by the presence of pentane insoluble $Me_3SiONa \cdot NaOH$ double salts [31]. Solutions of the moisture sensitive trialkylsiloxides were prepared in an inert atmosphere glove box and transferred by syringe through the autoclave fill port under a constant argon purge.

Triphenylsilane was distilled in vacuo (b.p. 150 °C/1 mmHg) immediately prior to use. The solvent for the kinetic runs, 1,4-dioxane, was purified by two consecutive distillations from sodium sand. The tristrimethylsilyl borate solvent (b.p. 174 °C/750 mmHg) used for the experiment in row 8 of Table 3 was prepared by the metathesis of trimethyl borate with trimethylsilanol according to an established procedure [32,33].

Kinetic method

The reactions were run in a glass reaction vessel equipped with a gas buret in a thermostated oil bath. Liquid samples were removed through a gas-tight rubber septum which was separated from the main reaction vessel by an isolation stopcock, except for the brief period of time required to remove a liquid sample with a hypodermic syringe. The reactions were followed spectrophotometrically on a Perkin-Elmer Model 1500 FTIR spectrometer. The triphenylsilane-triphenylsilanol dehydrocondensation reaction was effectively quenched upon removing the liquid samples at ambient temperature, as demonstrated by multiple scans at latter time periods. Hydrogen was identified by comparison of its gas chromatographic retention time with an authentic sample on a 3.5-ft spherocarb column at 40 °C and quantitated by the gas buret. As a general check of the gas buret, multiple determinations of triphenylsilane, 0.10 *M*, hydrolysis with water, 1.0 *M*, in piperidine solvent at 25 °C were followed by hydrogen evolution yielding first order rate constants of: 1.15, 0.98, 0.99, 0.90, 1.25, 1.07, and 1.19×10^{-4} s^{-1}, respectively, under conditions where the literature reports [34] 1.0×10^{-4} s^{-1}.

Hydrogenations

Reactions of hexamethyldisiloxane with hydrogen were conducted in a 300 ml Autoclave Engineers' vessel modified so that all components that contact the solution are made of pyrex glass. Trimethylsilyl hydride and methane were quantitated against authentic samples by gas chromatography on a 6-ft Porapak Q column programmed from 100 to 200 °C at 10° min^{-1}. In addition, trimethylsilane was independently confirmed by identification of its Si–H stretching frequency at 2114 cm^{-1}. Routine analyses of the solution phase for additional organosilicon compounds were performed gas chromatographically on a 50-ft BPI capillary column programmed from 40 to 280 °C. A high boiling organosilicon oil was produced concurrent with the loss of hexamethyldisiloxane from the solution phase; however, the identity of this oil was not established.

Acknowledgments

We thank Professor J. Halpern for helpful discussions throughout the course of this investigation. Support for this work was provided by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

References

1 R.J. Klingler, I. Bloom, and J.W. Rathke, Prepr.-Am. Chem. Soc., Div. Pet. Chem., 31 (1986) 61.
2 R.J. Klingler and J.W. Rathke, Organometallics, 5 (1986) 2569.
3 R.J. Klingler, I. Bloom, and J.W. Rathke, Organometallics, 4 (1985) 1893.
4 E. Lukevics and M. Dzintara, J. Organomet. Chem., 295 (1985) 265; a reviewer with 136 references.
5 R.L. Schowen and R. Bacon, Tetrahedron Lett., (1970) 4177.
6 C. Eaborn and I.D. Jenkins, J. Organomet. Chem., 69 (1974) 185.
7 K.O'Donnell, R. Bacon, K.L. Chellappa, R.L. Schowen, and J.K. Lee, J. Am. Chem. Soc., 94 (1972) 2500.
8 D.J. Hajdasz and R.R. Squires, J. Am. Chem. Soc., 108 (1986) 3139.
9 W.H. Stevenson, S. Wilson, J.C. Martin, and W.B. Farnham, J. Am. Chem. Soc., 107 (1985) 6340 and ref. cited therein.
10 C.L. Frye, G.A. Vincent, and W.A. Finzel, J. Am. Chem. Soc., 93 (1971) 6805.
11 A. Hosomi, H. Hayashida, S. Kohra, and Y. Tominaga, J. Chem. Soc., Chem. Commun., (1986) 1411.
12 J. March, Advanced Organic Chemistry, 3rd edit., Wiley-Interscience, New York, 1985, p. 344.
13 E. Weiss, K. Hoffmann, and H. Grützmacher, Chem. Ber., 103 (1970) 1190.

14 Reference 12, p. 189.
15 R. Walsh, Acc. Chem. Res., 14 (1981) 246.
16 W.S. Tatlock and E.G. Rochow, J. Am. Chem. Soc., 72 (1950) 528.
17 G. Eaborn and N.A. Stanczyk, J. Chem. Soc. Perkin Trans. 88, (1984) 2099.
18 J. Schindler and H. Schmidbaur, Angew. Chem. Int. Edit., 6 (1967) 683.
19 I. Ruidisch and M. Schmidt, Angew. Chem. Intern. Edit., 2 (1963) 328.
20 W.K. Wilmarth, J.C. Dayton, and J.M. Flournay, J. Am. Chem. Soc., 75 (1953) 4549.
21 S.L. Miller and D. Rittenberg, J. Am. Chem. Soc., 80 (1957) 64.
22 C. Walling and L. Bollyky, J. Am. Chem. Soc., 86 (1964) 3750.
23 J. Halpern, Annu. Rev. Phys. Chem. 16 (1965) 103 and ref. therein.
24 R.J. Jordan, C.S. Bajgur, and W.E. Basher, Organometallics, 6 (1987) 1041 and ref. cited therein.
25 A.W. Langer, Adv. Chem. Ser., 130 (1974) 1.
26 D. Cremer and E. Kraka, J. Phys. Chem., 90 (1986) 33.
27 B.R. James, Homogeneous Hydrogenation, Wiley-Interscience, New York, 1973, and ref. therein.
28 A. Yamamoto, Organotransition Metal Chemistry, Wiley-Interscience, New York, 1986, Chapter 6.
29 J.P. Collman, Acc. Chem. Res., 1 (1968) 136.
30 W.S. Tatlock and E.G. Rochow, J. Org. Chem., 17 (1952) 1555.
31 J.H. Hyde, O.K. Johannson, W.H. Daudt, R.F. Fleming, H.B. Laudenslager, and M.P. Roche, J. Am. Chem. Soc., 75 (1953) 5615.
32 M.G. Voronkov and V.N. Zgonnik, Zh. Obsh. Khim., 27 (1957) 1476.
33 E.W. Abel and Singh, J. Chem. Soc., (1959) 690.
34 H. Gilman, G.E. Dunn, H. Hartzfeld, and A.G. Smith, J. Am. Chem. Soc., 77 (1955) 1287.