Silicon Radicals. Relative Rates and Selectivity Ratios in the Radical Reactions of Silicon–Hydrogen Bonds with Carbon–Halogen Bonds

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Abstract: Relative rates of hydrogen abstractions by trichloromethyl radical from numerous silanes of varied structure have been performed and the reactivities correlated with structure. Electron-withdrawing groups retard the rate of hydrogen abstraction. Silanes have also been allowed to react with bromotrichloromethane, and from the selectivity of ratios (SiBr/SiCl) stabilities of the silyl radicals involved were derived.

In the late 1940's silicon radicals were postulated as intermediates in reactions involving addition of the silicon–hydrogen bond to olefins (hydrosilation) as catalyzed by organic peroxides and light[1,2] and by heat.[3] More recently, especially during the last decade, interest in the fundamental properties, reactivities, and general chemistry of silicon radicals has greatly intensified.[4]

Since no extensive systematic study of structure–reactivity relationships for silicon radical reactions had been reported, and because we considered that such a study would be important for future development of silicon radical chemistry, we have investigated and here report structure–reactivity relationships for the radical reactions of 26 different Si–H compounds of widely varied structure. In addition, selectivity ratios of 12 different silicon radicals with $BrCCl_3$ are reported.

In other radical reactivity studies, especially of carbon radicals, once a suitable source of a particular radical had been developed, its reactions with a carefully chosen series of hydrocarbons were studied. From the primary/secondary/tertiary selectivity ratios thus obtained, the radical could be placed in its proper position on the scale of radical reactivities. However, silicon radicals abstract hydrogen from hydrocarbons only with difficulty, due to unfavorable thermodynamics and prohibitively high activation energies.[5] Therefore this method could not be used for our purpose.

The relatively low bond dissociation energy of Si–H compared to C–H, $D[(\text{C–H}) - (\text{Si–H})] = \sim 25$ kcal/mol, suggests that carbon radicals should readily abstract hydrogen from Si–H compounds and that it should be possible to study relative rates of a variety of Si–H compounds with a suitable organic radical. In the gas phase, Kerr[6,7] and Thynne[8] have studied the reactivity of simple silanes toward methyl radical. Other gas-phase work involving only $SiHCl_3$ has also been reported.[9–11] In the liquid phase, reactions of Si–H compounds with alkyl halides are known[12–14] and the nature of the catalysis leaves little doubt that these reactions proceed by a free-radical chain reaction involving silicon radicals.

When the alkyl halide is carbon tetrachloride and the initiator is benzoyl peroxide, the chains are of moderate length (50–80); furthermore the reaction is fast, clean, and uncomplicated by side reactions. The mechanism proposed[15] is shown in eq 1–3. Because of its advantages, this system was chosen for our studies of the radical reactions of Si–H compounds. Pairs of silanes with varied structure were run in competition for the trichloromethyl radical and thus relative rates of hydrogen abstraction were obtained. The relative rate constants were calculated by the Ingold–Shaw equation (4) for competitive chain carrying steps in radical chain reactions involving the same attacking radicals. In the equation shown the $[\text{SiH}]_\sigma$ and $[\text{SiH}']_\sigma$ represent the initial concentrations of the two silicon hydrides and $[\text{SiH}]_f$, $[\text{SiH}']_f$ the final concentrations. If the structures of the competing silanes are varied in a systematic manner, the relationship between structure and reactivity can be ascertained. The results are reported in Table I. The substituted phenylsilanes (1–7) yielded rate constants which correlated well with the Hammett σ constants for the meta and para ring substituents with a ρ value of -0.54. Therefore, there is a definite polar effect and electron-withdrawing groups on the phenyl ring retard the rate of hydrogen abstraction.

$$R_3SiH + In \longrightarrow R_3Si\cdot + InH \tag{1}$$

$$R_3Si\cdot + CCl_4 \longrightarrow R_3SiCl + \cdot CCl_3 \tag{2}$$

$$R_3SiH + \cdot CCl_3 \longrightarrow R_3Si\cdot + CHCl_3 \tag{3}$$

$$\frac{k}{k'} = \frac{\log [\text{SiH}]_\sigma/[\text{SiH}]_f}{\log [\text{SiH}']_\sigma/[\text{SiH}']_f} \tag{4}$$

The negative value of the reaction constant is the expected result on the basis of the electrophilic nature of

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Table I. Relative Rates of Hydrogen Abstraction from Silanes by Trichloromethyl Radical[a]

1.	α-NpPhMeSiH	1.00	14.	(*m*-$CF_3Ph)_3SiH$	0.36
2.	α-Np-*m*-FPhMeSiH	0.64	15.	α-$NpPh_fMeSiH$[c]	0.18
3.	α-Np-*m*-MeOPhMeSiH	0.87	16.	$PhPh_fMeSiH$	0.28
4.	α-Np-*m*-$CF_3PhMeSiH$	0.57	17.	PhMeClSiH	0.25
5.	α-Np-*p*-MePhMeSiH	1.20	18.	$MeCl_2SiH$	0.13
6.	α-Np-*p*-$CF_3PhMeSiH$	0.51	19.	Cl_3SiH	0.11
7.	α-Np-*p*-MeOPhMeSiH	1.36	20.	PhMeFSiH	0.08
8.	$PhMe_2SiH$	0.83	21.	α-NpPhMeSiD	0.30
9.	*m*-CF_3PhMe_2SiH	0.47	22.	$Ph_3SiPhMeSiH$	7.1
10.	*p*-$MeOPhMe_2SiH$	1.11	23.	1-Silabicyclo[2.2.1]-heptane	0.40
11.	Ph_2MeSiH	1.00	24.	*neo*-$C_5H_{11}PhMeSiH$	0.88
12.	Ph_3SiH	1.47	25.	Ph_2SiH_2[b]	0.83
13.	$(PhCH_2)_3SiH$	0.38	26.	$Me(C_6H_{11})_2SiH$	1.20

[a] All reactions were run in refluxing carbon tetrachloride. [b] Corrected statistically. [c] Ph_f represents pentafluorophenyl.

the trichloromethyl radical and the electropositive character of the silicon atom. In the transition state the carbon atom would have a partial negative charge which the three electronegative chlorine atoms could readily stabilize, and the silicon atom would have some siliconium ion character. This can be represented by structure A. This is also consistent with the positive ρ^* of +0.26 and +0.29 for reaction of phenyldimethyl-

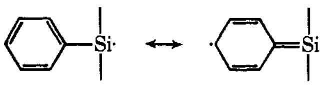
$$\overset{\delta+}{R_3Si}\cdots H\cdots \overset{\delta-}{CCl_3}$$

A

silane and triethylsilane with substituted trichloromethanes, $XCCl_3$.[15] The relatively small magnitude of the ρ value indicates that the above charge separation is not large. Our value of −0.54 is in accord with the ρ values very recently reported by Nagai[16] of −0.460, −0.372, and −0.453 for the limited series $PhSiMe_nH_{3-n}$ obtained under the same reaction conditions used in our study.

From Table I it is seen that replacement of a methyl by a phenyl enhances the rate of hydrogen abstraction (8, 11, 12). The phenyl group is known to have an electron-withdrawing polar effect and retardation of rate would have resulted if this were the dominant factor. However, the phenyl group can also exert an electron-releasing *resonance* effect toward an adjacent positive charge. Since the Hammett study showed that there is a partial positive charge on the silicon, the resonance effect can stabilize this charge. Thus, the energy of activation is lowered and rate acceleration is observed. However, when the resonance interaction is removed, as in the tribenzylsilane (13), by insertion of a methylene group between the silicon and the phenyl, the rate is retarded since only the polar effect of the phenyl is operative.

The possibility existed that the accelerating effect of the phenyl was due to the delocalization of the electron through the benzene ring, which would also lower the energy of activation for hydrogen abstraction (eq 5).



(5)

However, when the electron-acceptor capacity of the phenyl groups was enhanced by substitution with the electronegative trifluoromethyl group (14) or replacement with pentafluorophenyl groups (15 and 16), rate retardation instead of acceleration occurred. Thus, the resonance interaction pictured in eq 5 seems not to be of much importance in these reactions.

It is clear (17–19) that substitution of a chlorine directly on the silicon for a methyl or phenyl lowers the rate of hydrogen abstraction. This was expected from the polar effect since the chlorine is more electronegative than carbon. Substitution of a fluorine has a greater effect (20), consistent with its higher electronegativity.

From Table I when the α-naphthylphenylmethylsilane (1) was run in competition with its deuterio derivative (21), a primary kinetic isotope effect (K_H/K_D) of 3.4 resulted. Therefore, although there may not be enough breaking of the Si–H in the transition state for the activated complex to resemble the product, enough stretching of the bond has occurred to yield a substantial isotope effect. This is reasonable since the trichloromethyl radical is a fairly selective species. This value is similar to the isotope effect found in organotin radical hydride exchange reactions with carbon–halogen bonds ($K_H/K_D \cong 3$).[17] From Table I the disilane (22) is the fastest hydrogen donor. It is approximately 90 times more reactive than phenylmethylfluorosilane. This is readily explained by the electropositive nature of the β silicon atom which releases electron density to the silicon reaction center (eq 6). This would stabilize the

$$Ph_3Si \longrightarrow \overset{\delta+}{Si}\cdots H\cdots \overset{\delta-}{CCl_3} \qquad (6)$$

partial positive charge formed on the silicon undergoing the hydrogen abstraction and thus speed the reaction. It should be mentioned that when α-naphthylphenylmethylgermane was run in competition with the disilane, the germane underwent hydrogen abstraction at a much faster rate and was too fast to measure by the methods employed in the study. Thus the Ge–H bond is a much better hydrogen source in a radical reaction than the Si–H bond.

Finally from Table I it is seen that the bridgehead silane (23), 1-silabicyclo[2.2.1]heptane, is quite unreactive. Relative to acyclic compounds angle strain in the bridgehead system may be expected to result in increased p character of the ring silicon–carbon bonds and, therefore, increased s character of the Si–H bond. The effect is directionally the same as placing a highly electronegative substituent (such as Cl) on the silicon, and rate retardation is the expected result because electron withdrawal retards the rate.

The data of Table I reveal an interesting dominant polar effect of substituents on relative rates of radical reactions of Si–H compounds with trichloromethyl radical (except for phenyl which gives resonance stabilization of an adjacent partial positive charge). However, the relative rates in Table I will not reveal the relative order of stability of the derived radicals *unless the transition states of these reactions strongly resemble the silicon radicals themselves.* Since it has been shown that the Si–H bond is much more reactive than the C–H bond toward radicals such as methyl and trifluoromethyl,[7,8] it is possible that the transition state for eq 3 resembles R_3SiH more than $R_3Si\cdot$. To try to settle this point as well as to determine as definitively

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as possible an actual order of stability for silicon radicals another series of studies was undertaken.

It has been shown[18,19] that silyl radicals show selectivity in their reactions with different types of alkyl halides. The order of reactivities is tertiary > secondary > primary and Br > Cl > F. Therefore, the reactions of 12 different silanes of varied structure with bromotrichloromethane were studied. From the resulting selectivity ratios (SiBr/SiCl), and applying the usual inverse relationship[20] of reactivity and selectivity, it was hoped that a valid stability order for 12 silyl radicals could be established. The results are reported in Table II, where it is seen that the silanes exhibited marked selectivity in their reaction with bromotrichloromethane. The alkyl- and aryl-substituted silanes show similar selectivities in the range 2–3. However, as chlorine is substituted progressively on the silicon, the selectivity rises dramatically until trichlorosilane is reached, where bromine abstraction is the exclusive process, *i.e.*, a totally selective reaction. Therefore it appears that the trichlorosilyl radical is the most stable species. It is possible that the lone electron is stabilized by delocalization into the low-lying d orbitals of the chlorines.[21] This would be consistent with the findings of Kerr[7] that trichlorosilane donates hydrogen at the fastest rate when attacked by methyl radical in the gas phase. Methyl radical is a relatively neutral species compared to trichloromethyl, and is neither nucleophilic nor electrophilic. Thus, no polar effect masks the influence of the formed radical's stability on the rate of hydrogen abstraction. A polar factor would not adequately explain the enhanced selectivity of trichlorosilyl radical, for the highly electronegative pentafluorophenyl-substituted silanes show no dramatic increase in selectivity.

Table II. Reaction of Silanes with Bromotrichloromethane

Silane	SiBr/SiCl	Silane	SiBr/SiCl
1. α-NpPhMeSiH	2.2	7. $MeCl_2SiH$	8.2
2. Ph_2MeSiH	2.4	8. Cl_3SiH	Only SiBr
3. Ph_3SiH	2.3	9. PhC_6F_5MeSiH	2.9
4. $PhMe_2SiH$	2.1	10. α-NpC_6F_5MeSiH	3.0
5. $Ph_3SiPhMeSiH$	2.6	11. PhMeFSiH	6.5
6. PhMeClSiH	6.5	12. 1-Silabicyclo-[2.2.1]heptane	7.0

Finally the bridgehead silyl radical, 1-silabicyclo-[2.2.1]heptane, is quite selective in its reactivity with bromotrichloromethane. This is in sharp contrast to the findings in carbon bridgehead radical reactions with bromotrichloromethane using similar systems.[22,23] Carbon bridgehead radicals are very unselective in reaction with $BrCCl_3$. This selectivity is consistent with the known pyramidal structure of silyl radicals as shown by spectral[24] and stereochemical[25] evidence. No destabilization should occur when a silicon radical is constrained in this configuration as it is in the bridgehead system. However, in carbon radical chemistry the normal radical is near planar[26] and considerable destabilization and thus nonselectivity of reaction results when the radical is forced into a pyramidal configuration. The racemization[27] of the carbon radicals produced from optically active substrates is consistent with these observations. Cooper[21] has found similar variations of selectivities in reactions of methylchlorosilanes with *n*-hexyl chloride and cyclohexyl chloride. Again the trichlorosilyl radical was the most selective.

Experimental Section

Analyses of the products were performed by nmr and ir employing a Varian Model A-60A nmr and a Varian Model 1200-D flame ionization glpc equipped with a 10 ft × 1/8 in. SE 30 5% on Chromosorb G SS column. All compounds were identified by their nmr chemical shifts relative to TMS and by comparison of retention times of unknowns with those of authentic material.

Preparation of Substituted Phenyl-α-naphthylmethylsilanes. The general procedure for preparation of the XPh-α-NpMeSiH compounds is described.

In a 500-ml, three-necked flask equipped with a reflux condenser, dropping funnel, stirring bar, and a nitrogen inlet tube were placed 4.0 g (0.165 g-atom) of Mg turnings and 150 ml of anhydrous THF. The appropriate meta- or para-substituted bromobenzene (0.11 mol) in 110 ml of THF was added slowly over 0.5 hr with stirring and reflux from heat of reaction. The resultant dark-brown solution was stirred an additional 1 hr. α-Naphthyldimethoxymethylsilane, 26.0 g (0.11 mol), in 160 ml of THF was added rapidly and the solution refluxed overnight. Lithium aluminum hydride, 4.5 g (0.12 mol), was added with ice cooling, and the solution was stirred overnight. The reaction mixture was poured onto a slurry of ice, dilute acid (5%), and pentane, and the organic layer was washed three times with water and then dried over sodium sulfate. The solution was filtered and the solvent removed on the steam bath. The oil remaining was distilled through a Nester Faust semimicro spinning band distillation column yielding the appropriate substituted phenylsilane.

Hydrogen Abstraction Reactions. The procedure followed for all competitions are essentially identical and only one general description is described. In a 25-ml, round-bottomed flask equipped with a reflux condenser and a nitrogen inlet tube were placed about 5 mmol of each silane and 0.5 mmol of benzoyl peroxide in 10 ml of carbon tetrachloride. A nmr aliquot was removed and the solution refluxed an appropriate time for 25–60% completion of reaction (1–4 hr). A second aliquot was removed and the two tubes were analyzed by nmr analysis. Integration of the Si–H resonances determined the initial and final concentrations of the silanes from which the relative *k* was calculated. A duplicate run was made and the two relative rate constants were averaged. Excellent reproducibility was generally attained and the range divided by the mean was usually less than ±5%.

Reactions of Silanes with Bromotrichloromethane. The procedure followed for all the reactions of the silanes with bromotrichloromethane were identical and only one general description will be given. In a tube were placed 5 mmol of the silane and 0.5 mmol of benzoyl peroxide in 5 ml of bromotrichloromethane, and the tube was sealed under nitrogen. The tube was placed in an oil bath maintained at 77° for an appropriate time to allow for substantial reaction (1–24 hr). The tube was opened and an aliquot removed

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for nmr or glpc analysis. The amount of chloro- and bromosilane produced was measured by integration of the methyl nmr resonances of the silanes. If the silane contained no methyl group standard glpc techniques were employed to determine the ratio of $CHCl_3$/$HCBrCl_2$ formed. A duplicate run was made and the two selectivity ratios [SiBr]/[SiCl] were averaged. Reproducibility within ±5% was observed.

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Nature of the Electronic Interactions in Aryl-Substituted Polysilanes[1a]

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Abstract: The ionization potentials and half-wave reduction potentials of a series of α-naphthyl- and phenyl-substituted polysilanes have been determined and used to elucidate the nature of the electronic interactions between aryl and polysilanyl groups. It is shown that the relative energies of the σ and π electrons have a substantial influence on the energy and character of the highest occupied molecular orbital, and hence the electronic spectra of these compounds. The effect of extension of the $3d_\pi$ molecular orbital of the polysilane chain is found to be minimal.

Historically, interest in the electronic properties of polysilanes and the heavier group IV catenates was first stimulated by the report[2] of the anomalous ultraviolet absorption spectra of their phenyl derivatives. For example, whereas the phenylated monomers $(C_6H_5)_4M$, M = C, Si, Ge, Sn, and Pb, exhibit only a slightly perturbed ^1L_a transition (206–211 nm)[3] associated with the benzene π system, the absorption maxima of the dimeric derivatives $(C_6H_5)_3M\cdot M(C_6H_5)_3$, M = Si, Ge, Sn, and Pb, are strongly red shifted (230–246.5 nm). Hague and Prince[2a] originally favored assigning this absorption to a $\pi_{C=C} \rightarrow 3d(\pi)_{Si-Si}$ charge-transfer transition, where the π electron is excited to a molecular orbital derived from extended overlap of the adjacent Si-3d orbitals of the silicon chain (Figure 1a). Subsequently, however, spectroscopic analysis was complicated by the demonstration that the permethylated catenates also absorb in the ultraviolet (Table I),[4] and that the transition need not necessarily be directly associated with the benzenoid π electrons.

Table I. Absorption Maxima of Methyl- and Phenylpolysilanes

	Absorption, nm	
n	$Me(SiMe_2)_nMe$	$Ph(SiMe_2)_nPh$
2	193	236
3	216	243
4	235	250.5
5	250	257.5
6	260	265

In recent publications[4,5] the nature of the electron spectra of the permethylated polysilanes, $Me(Me_{2n}Si)Me$, has been discussed in some detail. The shift of the long wavelength maximum with chain length (n) has been shown[5b] to correlate linearly with the ionization potential (IP), *i.e.*, the energy of the occupied highest MO, which is primarily σ_{Si-Si} in character. In many respects the polysilanes resemble the homologous alkane series $H(H_2C)_nH$, and the fact that the polysilanes absorb at longer wavelength than the alkanes is at least partially explained by the differences in IP of the two homologous series. The nature of the excited state of the polysilanes is less clear, though the fact that cyclic polysilanes form delocalized radical anions,[6] whereas alkanes do not, does lend credence to the idea that the excited state may involve an extended MO derived from $3d_\pi$–Si overlap.[7] Considering the aryl-substituted polysilanes, the modified absorption spectra (Table I) can be adequately described in terms of a red shifted $\sigma_{Si-Si} \rightarrow 3d_{Si-Si}$ transition, where the excited state is stabilized by interaction of the $3d_{Si-Si}$ MO with the p–π^* MO of the aryl group (Figure 1b). This supports the concept of a delocalized $3d_{Si-Si}$ MO. On the other hand, it has also been pointed out[5b] that the ground state σ_{Si-Si}–p_π interaction must also be considered (Figure 1b), and equally well explains the spec-

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(1) (a) Work done in partial fulfillment of Ph.D. requirements of R. N. C. at Duke University. A portion of this work has been presented previously: Organosilicon Symposium, Pittsburgh, Pa., 1971. (b) Correspondence should be addressed to Research Triangle Institute.

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(7) This molecular orbital is unlikely to be pure Si-3d and most probably contains some admixture of Si-4p orbitals and σ^*_{Si-C} orbitals of appropriate symmetry. However, Si-3d serves as a convenient label.