

The substituent effect on the reactivity of silanes towards *tert*-butoxyl radicals*

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The absolute rate constant for the reaction of *tert*-butoxyl radicals with tris(trimethylsilyl)silane has been measured by a laser flash photolysis technique. The effect produced by the neighboring silyl groups in the abstraction of the hydrogen atom bound to silicon is discussed in relation to formation of other tri-substituted silicon-centered radicals. Additional kinetic data are presented together with the e.s.r. spectra of some pertinent radicals.

Résumé. — La technique de photolyse éclair par laser, a été utilisée pour mesurer la constante de vitesse de la réaction du radical *tert*-butoxyle sur le tris(triméthylsilyl)silane. L'influence des groupes silyle adjacents, sur la réaction d'arrachement de l'atome d'hydrogène de la liaison SiH, est discutée en relation avec la formation de radicaux silyle trisubstitués. Différentes données cinétiques sont présentées, ainsi que les spectres de RPE des radicaux intermédiaires les plus importants.

Introduction

Silanes which contain silicon-hydrogen bonds are known to react with *tert*-butoxyl radicals to form silyl radicals in a fast manner (1, 2). However, the effect produced by neighboring alkyl, phenyl, alkoxy and chlorine substituents on the formation of silyl radicals is still not clear (1). Thus, the lack of difference in the reactivities of phenylsilanes and alkylsilanes has been attributed to ineffective stabilization of the silicon-centered radicals by neighboring phenyl groups. Moreover, alkoxy group and chlorine atom deactivate and activate Si-H bond respectively although they have similar group electronegativity. These latter results were interpreted tentatively by invoking a bonding interaction between chlorine d orbitals and semioccupied p orbital on the silicon in the chlorine substituted silyl radicals, *i.e.*, (d-3p) π bonding.

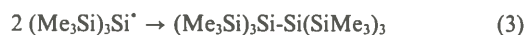
For a better understanding of this complex picture we decided to study the behaviour of (Me₃Si)₃SiH, a silane that has substituents with less electronegative character than alkyl groups and at the same time has a chance for a (d-3p) π bonding in the corresponding silyl radical. For such a study we utilized the techniques of *e.s.r.* spectroscopy and laser flash photolysis.

Results

LASER FLASH PHOTOLYSIS

The experiments were carried out by monitoring the transient absorptions produced when the samples were excited with the pulse (337.1 nm, ~8 ns, ~10 mJ) from a nitrogen laser. For example, when 0.13 M of (Me₃Si)₃SiH in a mixture of 1:4(v/v) di-*tert*-butyl peroxide : isooctane as solvent is irradiated, it leads to the formation of a transient species which exhibits a spectrum with continuous increasing absorption below ca. 350 nm and no maximum above 280 nm. This transient species decays with

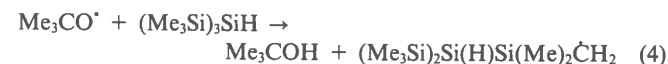
second-order kinetics. Under these conditions, the laser pulses are absorbed exclusively by the peroxide which undergoes a fast and efficient decomposition to yield *tert*-butoxyl radical (3). We propose that the above described spectrum is due to the free radical (Me₃Si)₃Si[•] generated in reaction 2 which decays by recombination according to reaction 3 and in agreement with the reported products study (4).



A plot of pseudo-first-order rate constant, derived from the buildup of the signal as a function of [(Me₃Si)₃SiH], yields $k_2 = (1.1 \pm 0.2) \times 10^8 \text{M}^{-1}\text{s}^{-1}$ at 296 K. An analysis of the second-order decay traces mentioned above yields $2k_3/\epsilon_{300 \text{ nm}} = 5.0 \times 10^6 \text{cm}^{-1}\text{s}^{-1}$.

The rate constant for the reaction of *tert*-butoxyl radicals with (Me₃Si)₃SiH can also be obtained by using diphenylmethanol as a probe. In this method, which has been described in considerable detail elsewhere (1, 5) one monitors the kinetics of the formation of Ph₂ĊOH radicals as a function of the concentration of added reagent. The method is quite accurate because the intense signal from Ph₂ĊOH makes detection quite easy. This approach led to $k_2 = (1.1 \pm 0.2) \times 10^8 \text{M}^{-1}\text{s}^{-1}$ at 295 K in a 1:2(v/v) mixture of benzene : di-*tert*-butyl peroxide as a solvent.

However, it should be noticed that both the kinetic procedures described yield absolute rate constants but do not distinguish between sites or modes of interaction of tris(trimethylsilyl)silane with *tert*-butoxyl radicals. Thus, there should be some attack at the methyl groups of silane (eq. 4). Assignment of the rate constant to a given path such as reaction 2 must be based on other knowledge. Thus, the rate constant for the reaction 5 is also obtained using diphenylmethanol as a probe.



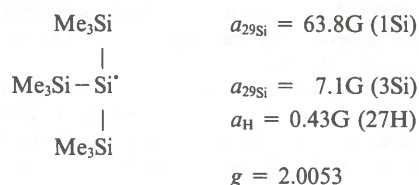
The value $k_5 = (7.4 \pm 1.7) \times 10^6 \text{M}^{-1}\text{s}^{-1}$ at 295 K shows that tetrakis(trimethylsilyl)silane is significantly less reactive towards *tert*-butoxyl than tris(trimethylsilyl)silane. Therefore, we estimate from the values of these two silanes that about 95 % of the attack occurs at the Si-H bond of (Me₃Si)₃SiH. Further support for this conclusion came from the *e.s.r.* experiments. Similarly, the rate constant for the reaction of *tert*-butoxyl radicals with hexamethyldisilane has been obtained at 295 K (see Table 2).

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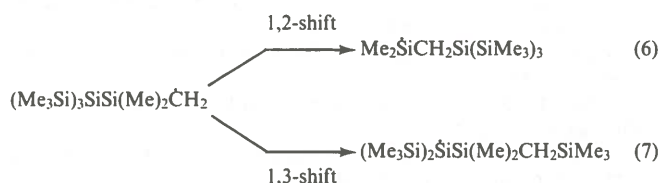
E.S.R. EXPERIMENTS

Photolysis of a solution of di-*tert*-butyl peroxide in $(\text{Me}_3\text{Si})_3\text{SiH}$ yields tris(trimethylsilyl)silyl radical whose spectrum shows the following parameters at 248 K :



No other transient species were observed.

Photolysis of a solution of $(\text{Me}_3\text{Si})_4\text{Si}$ and di-*tert*-butyl peroxide in cyclopropane or *tert*-butylbenzene and in temperature range of 153-373 K yields a transient species which exhibits an e.s.r. spectrum consisting of a triplet with hyperfine splitting of 20.10G and g -value of 2.0027, typical parameters for a carbon-centered radical of $-\dot{\text{C}}\text{H}_2$ type (see Table 2). However, at room temperature prolonged photolysis results in the generation of a second species whose spectrum consists of a doublet of doublets, *viz.*, $a_{\text{H}} = 18.25\text{G}$, $a_{\text{H}} = 35.85\text{G}$ and $g = 2.0028$. Certainly this last species derives from secondary reactions and structural assignment can be ambiguous. It is worth noticing that no evidence for the following 1,2- or 1,3-shift of a silyl group from silicon to carbon atom was found* :



* A 1,2-shift of a silyl group from silicon to carbon has been suggested to occur during the thermolysis of hexamethyldisilane at 873K. At 673K no thermal reaction of hexamethyldisilane occurred in agreement with the present results. (Shina K. and Kumada M., *J. Org. Chem.*, 1958, **23**, 139).

Consequently the rate constants for the unimolecular reactions 6 and 7 must be $< 10^3\text{s}^{-1}$ at 373 K.

Discussion

Comparison of the kinetic data in Table 1 reveals that neighboring trimethylsilyl group strongly activates the Si-H bond toward reaction with *tert*-butoxyl radicals. That is, the substitution of an alkyl group by a silyl group makes the reaction about 3 times faster, this effect being cumulative. From the electronegativity point of view, these results are in agreement with the fact that three ethoxy groups deactivate a neighboring Si-H bond. The magnitude of ^{29}Si hyperfine splittings through the series in Table 1 indicates that the radical center becomes more planar as the number of silyl groups increases. This change in geometry would be expected on the basis of Pauling's arguments that the structure of $\text{X}_3\text{A}^\bullet$ radicals depend on the electronegativity difference between A and X, since carbon is more electronegative than silicon (9). However, apart from electronegativity effects, the extra stabilization of the quasi-planar structure of tris(trimethylsilyl)silyl radicals may arise by a bonding interaction between β -silicon d orbitals and the semioccupied p orbital on the central silicon atom, *i.e.*, by $(d-3p)$ π bonding, similar to that suggested for trichlorosilyl (see Introduction). The trends of the g -values (*cf.* Table 1) support such a $(d-3p)$ π bonding interaction.

The enhancement in the reactivity at the α -position for hydrogen atom abstraction from Me_4Si relative to Me_4C has been attributed to a small degree of stabilization of α -silylalkyl radical relative to similar alkyl radical. Recently two kinetic studies (10, 11), based on indirect methods, have shown that the α -silyl substituent may stabilize an alkyl radical by 0.4 or 2.6 kcal mol $^{-1}$ (12). Such stabilization of α -silylalkyl radicals has been attributed to the delocalization of the unpaired electron either by $(d-2p)$ π -type interaction or by hyperconjugation. Our results reveal some interesting features concerning further silyl substitution in the β - and γ -position. Thus, radicals generated from hexamethyldisilane and tetrakis(trimethylsilyl)silane show a decrease in the spin density on the carbon bearing the unpaired electron (*cf.* Table 2); this is probably due to a better delocalization of the

TABLE 1

Rate constants for the reaction of *tert*-butoxyl radicals with some tri-substituted silanes and e.s.r. parameters for the corresponding radicals

Substrate	Radical	$a_{29\text{Si}}$, Gauss	g	k , $\text{M}^{-1}\text{s}^{-1}$ ^a	k , $\text{M}^{-1}\text{s}^{-1}$ ^b
Et_3SiH	$\text{Et}_3\text{Si}^\bullet$	181 ^c	2.0030	5.3×10^6 ^d	4.6×10^6
$\text{Me}_3\text{SiSi}(\text{Me})_2\text{H}$	$\text{Me}_3\text{SiSiMe}_2^\bullet$	137 ^c	2.0037	1.7×10^7 ^e	1.5×10^7
$(\text{Me}_3\text{Si})_3\text{SiH}$	$(\text{Me}_3\text{Si})_3\text{Si}^\bullet$	63.8	2.0053	1.1×10^8	1.0×10^8

(a) Overall reactivity at 296 ± 2 K ; solvent 1:4 (v/v) di-*tert*-butyl peroxide:benzene

(b) Corrected rate constants ; values represent the attack at the Si-H bond

(c) From reference 6

(d) From reference 7

(e) From reference 8

TABLE 2

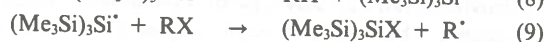
Rate constants for the reaction of *tert*-butoxyl radicals with some tetra-substituted silanes and e.s.r. parameters for the corresponding radicals

Substrate	Radical	a_{H} , Gauss	k , $\text{M}^{-1}\text{s}^{-1}$
Me_4Si	$\text{Me}_3\text{SiCH}_2^\bullet$	20.88 ^a	—
$\text{Me}_2\text{SiSiMe}_3$	$\text{Me}_3\text{SiSi}(\text{Me})_2\text{CH}_2^\bullet$	20.15 ^a	1.7×10^6
$(\text{Me}_3\text{Si})_4\text{Si}$	$(\text{Me}_3\text{Si})_3\text{SiSi}(\text{Me})_2\text{CH}_2^\bullet$	20.10	7.8×10^6

(a) From reference 13

odd-electron by Si-Si σ^* orbital relative to C-Si σ^* orbital in $\text{Me}_3\text{SiCH}_2^{\cdot}$ radical. Furthermore the H-atom abstraction from $(\text{Me}_3\text{Si})_4\text{Si}$ is twice as fast as from $\text{Me}_3\text{SiSiMe}_3$ (the k values are weighted by a factor of 1/2 and 1 respectively). This fact leads us to suggest that either anchimeric assistance by the β -silyl group (14) is greater in the polysilyl-substituted silane or that anchimeric assistance by γ -silyl group plays an important role.

Based on the present kinetic data silicon-hydrogen bond dissociation energies have recently been measured using a photoacoustic technique (15). The results, *viz.*, $\text{BDE}[\text{Et}_3\text{Si}-\text{H}] = 90.1$, $\text{BDE}[\text{Me}_3\text{Si}(\text{Me})_2\text{Si}-\text{H}] = 85.3$ and $\text{BDE}[(\text{Me}_3\text{Si})_3\text{Si}-\text{H}] = 79.0 \text{ kcal mol}^{-1}$, demonstrate that silicon-hydrogen bonds can be dramatically weakened by successive substitution of silyl groups at the Si-H function. In fact, the silicon-hydrogen bond in $(\text{Me}_3\text{Si})_3\text{SiH}$ is weak enough that the compound can be used as a free radical reducing agent. Preliminary work (16) shows that the reduction of alkyl halides, RX, to the hydrocarbon, RH, with tris(trimethylsilyl)silane is an efficient process. This reaction involves a two-step free radical chain process



Conclusions

Contrary to what is generally believed, the reactivities of silanes containing a silicon-hydrogen bond towards free radicals may be of a wide range. Thus, although the importance of delocalization of the unpaired electron in the alkyl radicals is essentially unimportant in the silicon congeners, the (d-3p) π -type bonding together with the electronegative character of the substituents can play a very important role.

Experimental part

MATERIALS

Tris(trimethylsilyl)silane and tetrakis(trimethylsilyl)silane were prepared by reaction of trichlorosilane with trimethylchlorosilane as described by Bürger and Kilian (17). Tris(trimethylsilyl)silane was purified by careful distillation followed by preparative g.l.c.; the purity before use was > 98 % by analytical g.l.c. All other reagents and solvents used in this work were commercial materials which were purified by standard methods before use.

PROCEDURES

The laser flash photolysis experiments were carried out under oxygen-free conditions using the pulse (337.1 nm, ~ 8 ns, up to ~ 10 mJ) from a Moletron UV 24 nitrogen laser for excitation. The experimental system has been interfaced with a PDP/03L computer that controls the experiment and provides suitable data gathering, storage, and hardcopy facilities. Complete details have been given elsewhere (18).

E.s.r. spectra were recorded on a Bruker EP 200 spectrometer equipped with an n.m.r. gaussmeter (field calibration), a frequency counter (g -factor determination), and a standard variable temperature device. A 1 kW high-pressure mercury lamp was used as UV light source. The experiments were carried out under oxygen-free conditions.

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