

1954

A study of organosilicon free radicals

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A STUDY OF ORGANOSILICON FREE RADICALS

by

Jay Stephen Curtice

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

Major Subject: Physical Organic Chemistry

Approved:

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INTRODUCTION

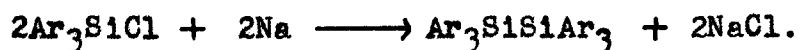
Much of the early work on organosilicon compounds was predicated on the expectation that the chemical behavior of carbon and silicon should be quite similar. Although this expectation was verified in a gross sense, it has become apparent that the rates of many reactions occurring at silicon atoms are very different from those of their carbon analogues, and that certain reactions unknown in carbon systems occur at silicon atoms. It has also been found that attachment of a silicon atom to a carbon skeleton will modify, to a limited extent, the behavior of the rest of the molecule.

The chemistry of organic free radicals has received intensive study, but reports of organosilicon free radicals are relatively rare. The purpose of this work was to study organosilicon free radicals in their role as reactive intermediates, and to gain information as to the similarities, and, particularly, the differences of the reactivities of silicon and carbon free radicals.

HISTORICAL

Hexaaryldisilanes as Analogues of Hexaarylethanes

Gomberg's preparation and characterization of triphenylmethyl¹ provided the impetus for several attempts to prepare an analogous triarylsilyl radical by similar means:



The first of these attempts was made by Schlenk and co-workers² who prepared hexaphenyldisilane from triphenylchlorosilane and sodium. These workers found no evidence of free radical activity in their product, in contrast with the highly unsaturated behavior of Gomberg's triphenylmethyl solutions. This work was repeated by Gilman and Dunn³ who confirmed the earlier work. In the same paper, Gilman and Dunn reported the successful synthesis of hexa-p-biphenyldisilane by the reaction of hexachlorodisilane and

¹M. Gomberg, Ber., 33, 3150 (1900); J. Am. Chem. Soc., 22, 757 (1900).

²W. Schlenk, J. Renning and G. Rackey, Ber., 44, 1178 (1911).

³H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 73, 5077 (1951).

p-biphenyllithium in ether; this compound, too, proved to be unreactive towards oxygen and iodine. Attempted preparations of the corresponding hexaaryldisilane by coupling tri-o-tolylchlorosilane⁴ or tri-1-naphthylchlorosilane⁵ in the presence of sodium gave no evidence of either formation of the substituted disilane or of free radical formation. Present work⁶ in these laboratories indicates that tri-o-biphenylchlorosilane is similarly unreactive toward sodium. Magnetic susceptibility measurements of a benzene solution of 1,1,2-triphenyl-1,2,2-tri-p-tolylidisilane⁷ showed no evidence of paramagnetic susceptibility, and hence, no evidence of dissociation into free radicals. Triphenylmethyltriphenylsilane⁸, prepared by the reaction of triphenylmethylsodium or triphenylmethyllithium with triphenylchlorosilane, shows no chemical evidence of a tendency to dissociate into free radicals.

⁴H. Gilman and G. N. R. Smart, J. Org. Chem., 15, 720 (1950).

⁵C. G. Brannen, Doctoral Dissertation, Iowa State College, 1951.

⁶K. Oita, Unpublished Studies, Iowa State College, 1954.

⁷H. Gilman and T. C. Wu, J. Am. Chem. Soc., 75, 3762 (1953).

⁸A. G. Brook, H. Gilman and L. S. Miller, J. Am. Chem. Soc., 75, 4759 (1953).

Thus, although in the hexaarylethane series, increasing the steric requirement of the aryl groups and increasing the possibilities for resonance stabilization of the radicals increases the dissociation of these compounds⁹, no combination of aryl groups likely to produce these effects in the silicon series has yet proved sufficient to cause noticeable free radical dissociation of hexaaryldisilanes under any conditions tested. It should be pointed out, however, that a search of the literature has brought to light no study of such a process at high temperatures, except for a study of the thermal dissociation of disilane itself¹⁰. These authors' data were consistent with the hypothesis of Si-Si bond fission to form $H_3Si\cdot$, and their subsequent formation of SiH_4 by a radical abstraction of hydrogen from disilane, thus initiating a chain. The decomposition was studied at temperatures of 314-360°, and an activation energy of 51.3 k. cal./mole was found for the decomposition process postulated. Stakeland¹¹ found an activation energy of 48.9 k. cal./mole in a similar study.

⁹W. A. Waters, "The Chemistry of Free Radicals," 2nd Ed., Clarendon Press, Oxford, 1948, Chapter III.

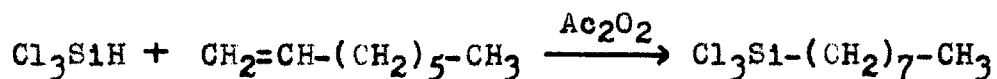
¹⁰H. J. Emeleus and C. Reid, J. Chem. Soc., 1021 (1939).

¹¹K. Stakeland, Trans. Faraday Soc., 44, 545 (1948).

In conclusion, it seems evident that aryl substituted disilanes show no evidence of a tendency to dissociate reversibly into free radicals under mild conditions, as do their carbon analogues. Such failure to dissociate may be due to lack of reorganization energy of the radical fragments, which may in turn be due to (a) lack of resonance energy of the species $\text{Ar}_3\text{Si}\cdot$, or (b) lack of steric strain in the substituted disilane. Both effects are demonstrably important in determining the degree of dissociation of hexaarylethanes^{9,12}.

Addition of Si-H Compounds to Olefins

Following the procedures of Kharasch and co-workers¹³ for the peroxide or ultraviolet light initiated addition of various compounds to olefins, Sommer, Pietrusza and Whitmore¹⁴ succeeded in adding trichlorosilane to 1-octene.

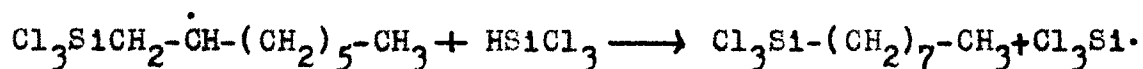
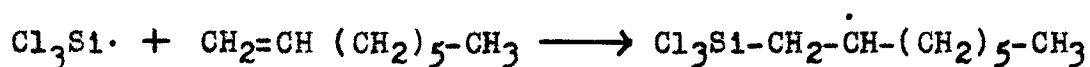
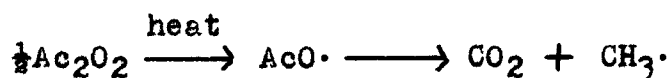


¹²H. Gilman, "Organic Chemistry, an Advanced Treatise," 2nd Ed., John Wiley and Sons, New York, 1933, Chapter VI.

¹³M. S. Kharasch, E. J. Jensen and W. H. Urry, Science, **102**, 128 (1945).

¹⁴L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, J. Am. Chem. Soc., **69**, 188 (1947); E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, J. Am. Chem. Soc., **70**, 484 (1948).

The reaction was carried out at 45°, with a six-fold molar ratio of trichlorosilane to 1-octene. Acetyl peroxide was present in catalytic amount, 0.025 mole per mole of trichlorosilane; the yield of 1-trichlorosilyloctane was 99 per cent, based on trichlorosilane. The same addition was successfully carried out by these authors by using ultraviolet light (a "weak" source) to initiate the reaction; the yield in this case was 24 per cent, based on trichlorosilane. These observations, together with the similarity of this addition reaction to the chloroform addition to olefins noted by Kharasch and co-workers¹³, led to a formulation of the reaction as a chain process¹⁴.



From 1947 to the present, several articles have appeared which have extended the application of this reaction to other olefins and other Si-H compounds. The results of these investigations are summarized in Table 1, as well as the results

Table 1
Free Radical Addition of Substituted Silanes to Olefins

Silane	Olefin	Product ^a	Temp.	Catalyst	% Yield	Ref.
HSiCl ₃	1-octene	CH ₃ (CH ₂) ₇ SiCl ₃	50-63	Ac ₂ O ₂	99	14
HSiCl ₃	1-octene	CH ₃ (CH ₂) ₇ SiCl ₃	47-54	u. v.	24	14
HSiCl ₃	2-octene	C ₈ H ₁₇ SiCl ₃	50-62	Ac ₂ O ₂	99	14
HSiCl ₃	2-methyl-1-heptene	CH ₃ (CH ₂) ₅ CH(CH ₃)- CH ₂ SiCl ₃	49-58	Ac ₂ O ₂	70	14
HSiCl ₃	2-methyl-1-propene	CH ₃ CH(CH ₃)CH ₂ SiCl ₃	25-30	u. v.	5	14
HSiCl ₃	2,3-dimethyl-2-butene	CH ₃ CH(CH ₃)C(CH ₃)- SiCl ₃	45-53	Ac ₂ O ₂	59	14
HSiCl ₃	2,4,4-trimethyl-1-pentene	C ₈ H ₁₇ SiCl ₃	49-50	Ac ₂ O ₂	9	14
HSiCl ₃	2,4,4-trimethyl-2-pentene	C ₈ H ₁₇ SiCl ₃	49-52	Ac ₂ O ₂	9	14
HSiCl ₃	1,1-dineopentyl-ethylene	C ₁₂ H ₂₅ SiCl ₃	50-60	Ac ₂ O ₂	1.6	14

^aWherever the structure of the product has not been established, the molecular formula is given.

Table 1 (Continued)

Silane	Olefin	Product	Temp.	Catalyst	% Yield	Ref.
HSiCl ₃	allyl chloride	C ₃ H ₆ SiCl ₄	43-47	Ac ₂ O ₂	20.4	14
HSiCl ₃	allyl chloride	C ₃ H ₆ SiCl ₄	41-43	u. v.	8.4	14
HSiCl ₃	2-methyl- 2-butene	C ₅ H ₁₁ SiCl ₃	41-45	Ac ₂ O ₂	24	14
HSiCl ₃	2-methyl- 2-butene	C ₅ H ₁₁ SiCl ₃	42-52	u. v.	64	14
HSiCl ₃	1-pentene	CH ₃ (CH ₂) ₄ SiCl ₃	70-100	Bz ₂ O ₂	44	15 ∞
HSiCl ₃	cyclohexene	C ₅ H ₁₁ SiCl ₃	70-100	Bz ₂ O ₂	30	15
HSiCl ₃	isobutylene	CH ₃ CH(CH ₃)CH ₂ SiCl ₃	70-100	Bz ₂ O ₂	10	15
HSiCl ₃	vinyltri- chlorosilane	Cl ₃ SiCH ₂ CH ₂ SiCl ₃	70-100	Bz ₂ O ₂	19	15
HSiCl ₃	allyltri- chlorosilane	Cl ₃ SiCH ₂ CH ₂ CH ₂ SiCl ₃	70-100	Bz ₂ O ₂	33	15
HSiCl ₃	acetylene	Cl ₃ SiCH ₂ CH ₂ SiCl ₃	70-100	Bz ₂ O ₂	3	15

¹⁵C. A. Burkhard and R. H. Krieble, J. Am. Chem. Soc., **69**, 2687 (1947).

Table 1 (Continued)

Silane	Olefin	Product	Temp.	Catalyst	% Yield	Ref.
HSiCl ₃	methyl oleate	C ₁₉ H ₃₇ O ₂ SiCl ₃	---	u.v.	22	16
HSiCl ₃	norpinene	C ₁₀ H ₁₇ SiCl ₃ (7-trichlorosilyl- p-menthene-Δ ₁)	---	Ac ₂ O ₂	--	17
HSiCl ₃	methyl ω -un- decylate	C ₁₂ H ₂₃ O ₂ SiCl ₃	---	Ac ₂ O ₂	75	18
HSiCl ₃	norpinene	C ₁₀ H ₁₈ Si ₂ Cl ₆ (bis(trichlorosilyl)- 2,7-p-menthane)	---	u.v.	--	19
HSiCl ₃	limonene	C ₁₀ H ₁₈ Si ₂ Cl ₆	---	u.v.	--	20
HSiCl ₃	limonene	C ₁₀ H ₁₇ SiCl ₃	---	u.v.	--	20

¹⁶R. Calas and N. Duffant, Bull. Soc. chim. France, 792 (1953).

¹⁷R. Calas and E. Frainnet, Bull. Soc. chim. France, 241 (1952).

¹⁸N. Duffant and R. Calas, Bull. Soc. chim. France, 241 (1952).

¹⁹E. Frainnet, Bull. Soc. chim. France, 792 (1953).

²⁰R. Calas, E. Frainnet and J. Valade, Bull. Soc. chim. France, 792 (1953).

Table 1 (Continued)

Silane	Olefin	Product	Temp.	Catalyst	% Yield	Ref.
HSiCl ₃	acetylene	Cl ₃ SiCH ₂ CH ₂ SiCl ₃	80	Bz ₂ O ₂	--	21, 22
HSiCl ₃	α-pinene	not identified	60-96	Bz ₂ O ₂	--	23
HSiCl ₃	vinyltrichloro- silane	Cl ₃ SiCH ₂ CH ₂ SiCl ₃	100	Ac ₂ O ₂	--	24
HSiCl ₃	allyltrichloro- silane	Cl ₃ Si(CH ₂) ₃ SiCl ₃	100	Ac ₂ O ₂	--	24
HSiCl ₃	1-pentyne	1-pentenyl-1- trichlorosilane	80	Bz ₂ O ₂	31	25
CH ₃ SiHCl ₂	1-pentene	1-pentylmethyldi- chlorosilane	70-100	Bz ₂ O ₂	10	15
CH ₃ SiHCl ₂	2-pentene	2-pentylmethyldi- chlorosilane	70-100	Bz ₂ O ₂	21	15

²¹R. H. Krieble, U. S. Patent 2,510,642 C. A., 44, 9473 (1950) .

²²British Thompson-Houston Company, British Patent 663,740 C. A., 46, 11228 (1952) .

²³L. O. Goldblatt and D. M. Oldroyd, U. S. Patent 2,533,240 C. A., 45, 2262 (1952) .

²⁴British Thompson-Houston Company, British Patent 661,094 C. A., 46, 5365 (1952) .

²⁵C. A. Burkhard, J. Am. Chem. Soc., 72, 1402 (1950).

Table 1 (Continued)

Silane	Olefin	Product	Temp.	Catalyst	% Yield	Ref.
CH ₃ SiHCl ₂	vinyltrichloro- silane	"product"	100	Ac ₂ O ₂	--	23
<i>n</i> -PrSiHCl ₂	1-octene	"impure product"	50	Ac ₂ O ₂	6	14
Et ₂ SiH ₂	1-octene	monosubst. product, not purified	50	Ac ₂ O ₂	"fair"	14
Et ₂ SiHCl	methyl 9- undecylate	Et ₂ SiCl(CH ₂) ₁₀ CO ₂ CH ₃	---	u. v.	--	16
Ph ₃ SiH	9-undecylenic acid	Ph ₃ Si(CH ₂) ₁₀ CO ₂ H	75	Bz ₂ O ₂	96	26
Ph ₃ SiH	ethyl 9-un- decylenate	Ph ₃ Si(CH ₂) ₁₀ CO ₂ C ₂ H ₅	--	Bz ₂ O ₂	--	26
Ph ₃ SiH	1-octene	Ph ₃ Si(CH ₂) ₇ -CH ₃	75	Bz ₂ O ₂	38	27
Ph ₃ SiH	1-dodecene	Ph ₃ Si(CH ₂) ₁₁ CH ₃	70	Bz ₂ O ₂	65	28
Ph ₃ SiH	1-tetradecene	Ph ₃ Si(CH ₂) ₁₃ CH ₃	70	Bz ₂ O ₂	90	28
Ph ₃ SiH	1-hexadecene	Ph ₃ Si(CH ₂) ₁₅ CH ₃	70	Bz ₂ O ₂	45	28
Ph ₃ SiH	1-octadecene	Ph ₃ Si(CH ₂) ₁₇ CH ₃	70	Bz ₂ O ₂	70	28

26G. N. Gadsby, Research (London), 3, 338 (1950).

27R. Fuchs, Unpublished studies, Iowa State College, 1954.

28H. Merten, Unpublished studies, Iowa State College, 1954.

of some unpublished studies carried out by others in these laboratories. The procedures and conditions for all these addition reactions are essentially similar to those given in the above example, with the exception of the variation in the method of initiation. No addition resulted from either the ultraviolet or peroxide initiated reaction of olefins with triethoxysilane¹⁴, silicon tetrachloride¹⁴, or di-*n*-propylchlorosilane¹⁵. In general, branching close to the olefinic linkage reduces the yield of adduct¹⁴.

Workers at Dow-Corning Corporation²⁹ have succeeded in adding a number of Si-H compounds to a variety of olefins by using pressure reactors and temperatures up to 400° in the absence of any catalyst. Although these additions proceed to give the same type of compounds obtained from the radical addition reactions, they were not listed in Table 1 along with the more clearly demonstrated radical additions. This latter method does, however, afford high conversions to useful intermediates, and may prove an important source for organosilicon synthetic materials.

Similar addition reactions have succeeded with triphenylgermane and 1-octene, by benzoyl peroxide catalysis as well as by ultraviolet irradiation²⁷. Triphenyltin hydride did

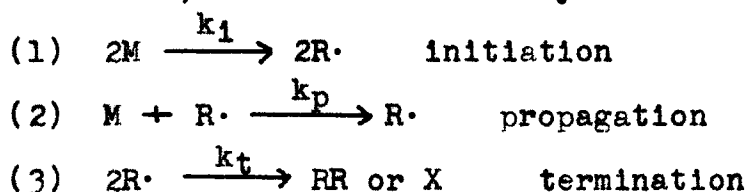
²⁹A. J. Barry, L. DePree, J. Gilkey and D. E. Hook, J. Am. Chem. Soc., 69, 2916 (1947).

not undergo the addition, but disproportionated to tetraphenyltin under the conditions of the experiment²⁷.

In summary, it seems clear that compounds containing an Si-H bond can take part in a free radical chain reaction of the type elucidated by Kharasch and co-workers¹³. This process can be best explained by the hypothesis of an intermediate, reactive chain carrying silyl radical.

Chain Transfer as a Measure of Radical Reactivity

The following scheme has been generally accepted as representing the course of a free radical polymerization of vinyl monomers, initiated thermally³⁰:



The symbols have these meanings: M, a monomer molecule; R·, a free radical, the growing polymer chain; X, termination products other than the coupling product (e.g., an alkane and an alkene, formed by disproportionation between the two

³⁰ For a general review of this field, see P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953; for a review of styrene polymerization, see R. H. Boundy and R. F. Boyer, "Styrene, its Polymers, Copolymers and Derivatives," Reinhold, New York, 1952.

$R \cdot$'s); k_i , k_p , k_t , the rate constants for the initiation, propagation, and termination processes respectively. From these expressions, equations can be derived which fit the experimental rate data for vinyl polymerization. Necessary assumptions are³⁰:

- (a) "At all stages of the polymerization, the reactivity of every like functional group is the same.";
- (b) The $R \cdot$ radicals are short-lived and of such small concentration that a steady-state treatment of the kinetics of the polymerization process is justified.

These equations and assumptions lead to a rate law of the form,

$$\frac{d[M]}{dt} = k' [M]^2 ,$$

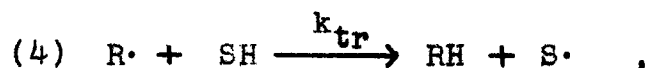
which agrees with experimentally determined rates.

Dilution of a vinyl monomer in a polymerization process generally causes a lowering of the molecular weight of the polymer³¹. Flory³² proposed a "chain transfer" as an

³¹H. Stautinger and L. Schwalbach, Ann., 488, 8 (1931).

³²p. J. Flory, J. Am. Chem. Soc., 59, 241 (1937).

explanation of this effect. In such a process, the growing polymer chain would transfer its reactive center to another molecule, thus terminating its own growth, but starting a new chain which would grow at the same rate until it was either terminated or transferred. One such process he proposed was a hydrogen abstraction reaction from the solvent, or transfer agent:



where SH represents the solvent. If the species $S\cdot$ were to continue to initiate polymer chains with high efficiency, the rate of polymerization would not be affected, but the molecular weight of the polymer would be decreased.

Mayo³³ derived a quantitative expression for this effect, essentially as follows:

- (a) The degree of polymerization, \bar{P} , can be expressed as the rate of chain growth divided by the total rate of termination of the growth of the polymer chain. In terms of the processes defined on page 12 and the chain transfer process, page 14, this expression is:

³³F. R. Mayo, J. Am. Chem. Soc., 65, 2324 (1943).

$$\bar{P} = \frac{k_p [R\cdot] [M]}{k_{tr} [R\cdot] [SH] + k_t [R\cdot]^2 + k_4 [R\cdot] [M]},$$

where k_{tr} represents the rate constant for chain transfer with monomer.

- (b) The term $[R\cdot]$ can be evaluated by means of the steady-state assumption as $(k_i/k_t)^{1/2} [M]$ provided the $[S\cdot]$ does not build up a high concentration and induce an abnormally high amount of radical-radical termination, or other complicating factors. The former condition is easily diagnosed experimentally, since the total rate of polymerization will be reduced, and SH will function as an inhibitor rather than as a chain transfer agent.
- (c) If the expressions in (a) and (b) are combined, the expression

$$\frac{1}{\bar{P}} = \frac{k_{tr} [SH]}{k_p [M]} + \frac{k_i k_t^{1/2} + k_4}{k_p}$$

results.

- (d) Substituting $C = k_{tr}/k_p$, and noting that for $[SH] = 0$, $1/\bar{P} = 1/\bar{P}_0$, where \bar{P}_0 is the degree of polymerization of the undiluted monomer, we have

$$\frac{1}{\bar{P}} = c \frac{[SH]}{[M]} + \frac{1}{\bar{P}_0}$$

Similar expressions have been similarly derived for photoinitiated and peroxide initiated polymerization.

The symbol "C" was defined by Mayo as the characteristic "transfer constant" of the solvent. The transfer constant was evaluated by plotting the ratio $[SH]/[M]$ against the reciprocal degree of polymerization of polystyrene, for conversions of ten per cent or less. Linear plots did indeed result, confirming the validity of the treatment³³⁻⁴⁰.

Average molecular weights of the polystyrenes formed at varying $[SH]/[M]$ ratios were determined by measuring their intrinsic viscosities in benzene; these intrinsic viscosities were related to the molecular weights determined by end-group

³⁴R. A. Gregg and F. R. Mayo, J. Am. Chem. Soc., 70, 2373 (1948).

³⁵R. A. Gregg and F. R. Mayo, Disc. Faraday Soc., 2, 328 (1947).

³⁶F. R. Mayo, J. Am. Chem. Soc., 70, 3689 (1948).

³⁷R. A. Gregg, D. M. Alderman and F. R. Mayo, ibid., 70, 3740 (1948).

³⁸F. R. Mayo, R. A. Gregg, and M. S. Matheson, ibid., 73, 1691 (1951).

³⁹R. A. Gregg and F. R. Mayo, ibid., 75, 3530 (1953).

⁴⁰F. R. Mayo, ibid., 76, 6133 (1954).

analysis and osmotic pressure measurements by equations of the form:

$$[\eta] = KM^a ,$$

where $[\eta]$ symbolizes the intrinsic viscosity of the polymer in a suitable solvent; M , the average (number average) molecular weight; K and a , experimentally determined constants.

In Table 2, taken from the data of Mayo and co-workers³⁵, there are listed values of transfer constants of some solvents at 60° and 100°³⁵.

The value of the chain transfer constant has been shown to be dependent on the resonance stabilization of the S· radical formed^{35,39} and on the polar nature of the reactants^{41,42}. Rationalization of the first effect follows naturally from a consideration of a transition state for the chain transfer reaction in which the S· radical is partly formed:



⁴¹F. R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).

⁴²C. Walling, J. Am. Chem. Soc., 70, 2561 (1948).

Table 2
Chain Transfer Constants of Various Solvents
in Styrene Polymerization

Solvent	Transfer constant $\times 10^5$	
	60°	100°
Benzene	0.15	1.84
<u>t</u> -Butylbenzene	0.6	5.5
Toluene	1.25	6.45
Ethylbenzene	6.7	16.2
<u>i</u> -Propylbenzene	8.2	20.0
Diphenylmethane	23	42
Triphenylmethane	35	80
Fluorene	750	1240
Pentaphenylethane	200,000	---
Cyclohexane	0.24	1.6
<u>n</u> -Heptane	4.4	9.5
Decalin	4	---
Carbon tetrachloride	900	1810

The odd electron is considered to be distributed between the "R" and "S" fragments, and any delocalization of the electron at the site of the "S" fragment would result in lowering the energy of the transition state, and hence, a larger chain transfer constant should be observed. Similarly, charge transfer in the transition state would have the same result³⁹. From Table 2, it can be seen that the magnitude of the chain transfer constant grows with increasing resonance stabilization of the S· species, for those solvents in which a carbon-hydrogen bond would be expected to be the point of attack. Carbon tetrachloride serves as an example of a molecule which should be an electron donor with respect to a styryl radical, and which does have a large chain transfer constant.

In summary, chain transfer constants are a convenient source of information about the reactivity of compounds toward free radicals, both polar effects and stabilization energy of the free radical formed by chain transfer seem to be important in determining the magnitude of the chain transfer constant.

Other Reported Silyl Radicals

A recent article⁴³ reports the reaction of tri-(diethylamino)-bromosilane with sodium at 150° to form tri-(diethylamino)-silane; 42 per cent of the bromo compound was converted to the silane, and 58 per cent of the unreacted bromo compound was recovered. The authors proposed a mechanism involving the formation of a tri-(diethylamino)-silyl radical, and its subsequent reaction with a "R-H" compound to produce the tri-(diethylamino)-silane.



The "RH" species is presumably the bromosilane itself, since the authors report no solvent for the reaction. They mention the formation of "high molecular products" attendant upon the formation of the silane, but no details of the isolation or characterization of such a product are given.

⁴³H. Brederveld, T. J. W. van Thoor and H. I. Waterman, Research (London), 7, S29 (1954).

Kraus and Eatough⁴⁴ have reported the isolation of a stable, white crystalline compound from the reaction of triphenylbromosilane and lithium in ethylamine. This compound was reported by these authors to undergo dimerization to hexaphenyldisilane on heating, and to add one equivalent of lithium in ethylamine to give a red solution characteristic of triphenylsilyllithium. On the basis of these observations, and silicon and nitrogen analysis, Kraus and Eatough assigned the compound the structure of triphenylsilyl ethylamine, or $(C_6H_5)_3Si \cdot NH_2CH_2CH_3$. This structure represents a "solvated" free radical.

Benkeser and co-workers⁴⁵ attempted to repeat these experiments. They were able to isolate a compound similar to the one described by Kraus and Eatough, as a product of the same reaction, but were unable to repeat the dimerization under heating. The compound isolated by Benkeser and co-workers proved to be triphenyl-N-ethylaminosilane, which they believed to be identical with the compound prepared by the earlier workers. Wu⁴⁶ of these laboratories also attempted the repetition of Kraus and Eatough's observations. He was

⁴⁴C. A. Kraus and H. Eatough, J. Am. Chem. Soc., 74, 5699 (1952).

⁴⁵R. A. Benkeser, R. E. Robinson and H. Landesman, J. Am. Chem. Soc., 74, 5699 (1952).

⁴⁶T. C. Wu, Doctoral Dissertation, Iowa State College, 1952.

able to prepare the compound described by these workers and by Benkeser and co-workers, but he found no evidence of free radical activity of the compound so prepared. Thus, serious doubt may be entertained as to the authenticity of the observations reported by Kraus and Eatough of the "solvated" triphenylsilyl free radical.

EXPERIMENTAL

Preparation and Purification of Materials

Preparation of triphenylsilane⁴⁷. Thirty-eight and seven-tenths grams (1.02 moles) of crushed lithium aluminum hydride was added to a dry, nitrogen filled 5 l. three-necked round-bottomed flask equipped with a blade stirrer, a reflux condenser, and an addition funnel. Three hundred ml. of diethyl ether which had been dried over calcium hydride was added, and the mixture stirred vigorously for 1-2 hours. To the resulting slurry was added 600 g. (2.03 moles) of Dow-Corning (purified grade Lot P-321) triphenylchlorosilane dissolved in 3 l. of dried diethyl ether, at such a rate as to promote gentle refluxing of the ether. After the addition was completed, the mixture was stirred and refluxed for 14 hours. At the end of this period, 110 ml. of ethyl acetate was added to destroy the excess lithium aluminum hydride. The ether layer was removed by filtration, and dried over anhydrous calcium sulfate. The ether, alcohol and ethyl acetate were removed by distillation, and the residue vacuum distilled at 1-2 mm. to yield a fraction boiling at 171-186^o; this fraction

⁴⁷H. Gilman and G. E. Dunn, J. Am. Chem. Soc., 72, 2178 (1950).

(410 g.) solidified on standing to yield a white solid melting at 43-47°. The crude yield (77.6 per cent of the theoretical, based on triphenylchlorosilane) was crystallized from methanol; the resulting material was vacuum dried at room temperature for 24 hours to yield 365 g. (69 per cent) of material melting at 43.8-45.0°. An infrared absorption spectrum of the product showed identity with previous spectra of authentic triphenylsilane, and indicated no trace of triphenylsilanol or hexaphenyldisiloxane impurity. Several similar preparations of triphenylsilane were carried out in this fashion. The yields of purified material varied from 69 to 86 per cent. Vigorous stirring was found to improve the yield. The usual precautions were observed in the use of lithium aluminum hydride⁴⁸.

Preparation of triethylsilane⁴⁹. To a 1 l. round-bottomed three-necked flask, equipped as described in the preceding experiment, was added 24.78 (0.650 mole) of lithium aluminum hydride, and 300 ml. of diethyl ether. The ether had been dried over calcium hydride. After the resulting slurry had been stirred for 1-2 hours, 198 g. (1.32 moles) of triethylchlorosilane (Dow-Corning, purified grade) dissolved in 100 ml. of dried diethyl ether was added at a rate sufficient to

⁴⁸W. G. Brown, Chapter X in "Organic Reactions," VI, R. Adams, Ed., John Wiley and Sons, Inc., New York, 1951.

⁴⁹H. Gilman, R. K. Ingham and A. G. Smith, J. Org. Chem., 18, 1743 (1953).

promote gentle refluxing of the ether. The stirring and refluxing was continued for 16 hours. The reaction mixture was then hydrolyzed, first with wet ether, and then with 95 per cent ethanol. The ether layer was immediately removed and dried over anhydrous calcium sulfate. The ether was flash distilled from the solution, and the residue fractionated on a glass helix-packed column, one meter in length and 1 cm. in diameter. The reflux ratio was more than 5:1 throughout the distillation. Fractions boiling from 107.0-.08.5° were combined to give 130 ml. of triethylsilane, $n_D^{25} = 1.4109$.

Chlorobenzene. Chlorobenzene (Matheson Chemical Company) was distilled through a one meter helix-packed column. Some batches were distilled through a 1.5 meter bubble-cap solvent column.

Di-tert-butyl peroxide. This material was kindly furnished by the Shell Chemical Corporation. It was distilled through a 44 plate center-rod column (b.p. 48.1-49.6° at 82-85 mm.) before use.

Styrene. Styrene (Eastman white label, "stabilized") was washed several times with 5 per cent aqueous sodium hydroxide, and subsequently shaken with portions of distilled water until the washings showed a neutral reaction to litmus. Anhydrous calcium chloride was added, and the dried material distilled through a 30 cm. Vigreux column, at reduced pressure.

The middle cut boiling at 38-39° at 10-11 mm. was collected for use and stored at 5°. The styrene was used within 24 hours after the distillation.

Chain Transfer Constants of Organosilanes

The chain transfer constants of triphenylsilane and triethylsilane were determined at 70 and 80° after the method of Mayo³³. Styrene and the silicon compound were introduced into pyrex test tubes with necks constricted to facilitate the vacuum sealing operation. The solutions were degassed by alternately freezing and thawing the contents of the tubes under vacuum. The contents of the tubes were then refrozen, and the tubes sealed under vacuum. The tubes were then introduced into one of the constant temperature baths for lengths of time depending on the silane-styrene ratio. After the proper reaction time, the tubes were removed, the reaction was quenched by cooling, the tubes were broken, and their contents were washed into 200 ml. of methanol. The precipitated polystyrene was isolated by decantation and/or filtration, and the polystyrene redissolved in about 50 ml. of benzene. The benzene solution was slowly poured into 200 ml. of methanol, thus reprecipitating the polystyrene. The resulting polystyrene precipitates were again filtered,

redissolved, and reprecipitated. Finally, the polystyrene samples were filtered into weighed sintered glass crucibles, dried in vacuo at 40-48° for periods of about 24 hours, and weighed. Table 3 summarizes the data thus obtained on the polystyrene fractions.

In addition to those polymerizations listed in Table 3, bulk polymerizations of undiluted styrene were run at both 70.00 and 80.05°. The 70° sample proceeded to 11.8 per cent polymerization in 48 hours, the 80° samples, to 11.4 and 10.7 per cent in 22 hours.

Each polystyrene sample was dissolved in benzene, and the time of flow through an Ostwald-Fenske viscometer determined for several dilutions of the original sample. These viscosities were measured at 29.98-.02°, and all flow times were greater than 150 seconds. The specific viscosities of the solutions, defined by the relation

$$\eta_{sp} = \frac{\text{time of solvent flow} - \text{time of solution flow}}{\text{time of solvent flow}}$$

could then be calculated. It has been found²⁵ that a plot of (η_{sp}/c) vs. c , where c is the concentration of the polystyrene solutions expressed in grams of polystyrene per ml. of solution, gives straight lines which may be extrapolated to zero concentration. The intercept so determined

Table 3
Polymerization of Styrene Diluted by Trisubstituted Organosilanes

Run	Temp. ^a (°C)	Silane	Moles silane x 10 ³	Moles styrene x 10 ³	Weight polystyrene (g.)	Time (hours)	% Polym.
1	70.00	Ph ₃ SiH	42.5	43.15	0.805	85	17.8
3	70.00	Ph ₃ SiH	21.2	43.15	0.608	67	13.5
4	70.00	Ph ₃ SiH	10.6	43.15	0.600	49	13.3
5	80.05	Ph ₃ SiH	21.2	43.15	0.535	27	11.9
6	80.05	Ph ₃ SiH	15.9	43.15	0.598	26	13.3
7	80.05	Ph ₃ SiH	10.6	43.15	0.600	25	13.3
8	80.05	Ph ₃ SiH	5.3	43.15	0.605	23	13.4

^aTemperatures were maintained to within 0.02° of the values stated.

Table 3 (Continued)

Run	Temp. ^a (°C)	Silane	Moles silane x 10 ³	Moles styrene x 10 ³	Weight polystyrene (g.)	Time (hours)	% Polym.
9	70.00	Et ₃ SiH	34.5	43.15	0.479	85	10.6
10	70.00	Et ₃ SiH	18.9	43.15	0.435	60	9.7
11	70.00	Et ₃ SiH	6.30	43.15	0.378	48	8.4
12	70.00	Et ₃ SiH	3.15	43.15	0.359	48	8.0
13	80.00	Et ₃ SiH	12.58	43.15	0.479	24	10.6
14	80.00	Et ₃ SiH	6.30	43.15	0.428	24	9.5
15	80.00	Et ₃ SiH	3.15	43.15	0.465	22	10.3
16	80.00	Et ₃ SiH	1.58	43.15	0.447	22	9.9

is called the intrinsic viscosity of the solute⁵⁰, and is commonly given the symbol $[\eta]$. A number of workers³⁰ have established empirical logarithmic relationships between the quantity $[\eta]$ and number average molecular weights of polystyrene samples. The formula selected for use in this work (given below) is that of Mayo, Gregg and Matheson³⁸. This relation has been checked by the above named workers with both osmotic pressure and end-group methods of evaluation of average molecular weights of polystyrene fractions.

$$\bar{M} = 104\bar{P} = 178000 [\eta]^{1.37}$$

Here \bar{M} represents the number average molecular weight; \bar{P} , the degree of polymerization, and $[\eta]$, the intrinsic viscosity of the polystyrene in benzene at 30°.

The $[\eta]$ values were determined as described above, and the chain transfer constants were determined by measuring the slope of the line obtained by plotting the reciprocal of the degree of polymerization against the silane to styrene molar ratio. Table 4 summarizes these calculations, and Figure 1 shows such plots for triphenylsilane and triethylsilane, both at 70°.

⁵⁰E. O. Kraemer, Ind. Eng. Chem., 30, 1200 (1938).

Table 4

Intrinsic Viscosities and Chain Transfer Constants of Polystyrene Reactions

Run	Temp. (°C)	Silane	$[\eta]$ at 30° in benzene	$\bar{M} \times 10^{-5}{}^a$	$1/\bar{P} \times 10^3{}^b$	$\frac{[SH]}{[M]}{}^c$	$C \times 10^4{}^d$
1	70.00	Ph ₃ SiH	0.270	0.266	3.91	0.986	33.4±1.2
3	70.00	Ph ₃ SiH	0.468	0.627	1.66	0.492	
4	70.00	Ph ₃ SiH	0.700	1.092	0.95	0.246	
5	80.05	Ph ₃ SiH	0.395	0.499	2.09	0.492	36.8±1.8
6	80.05	Ph ₃ SiH	0.507	0.702	1.48	0.369	
7	80.05	Ph ₃ SiH	0.615	0.936	1.11	0.246	
8	80.05	Ph ₃ SiH	0.743	1.185	0.88	0.167	

^aNumber average molecular weights, calculated by means of the formula $\bar{M} = 178000[\eta]^{1.37}$.

^bReciprocal degree of polymerization, calculated as $104.1/\bar{M}$, where 104.1 is the molecular weight of styrene.

^cThe symbol $[SH]/[M]$ represents the molar ratio of silane to styrene, or "solvent" to "monomer".

^dChain transfer constant.

Table 4 (Continued)

Run	Temp. (°C)	Silane	$[\eta]$ at 30° in benzene	$\bar{M} \times 10^{-5a}$	$1/\bar{P} \times 10^3b$	$\frac{[SH]^c}{[M]}$	$C \times 10^4d$
9	70.00	Et ₃ SiH	1.54	3.24	0.321	0.798	2.44 ± 1.12
10	70.00	Et ₃ SiH	1.87	4.17	0.250	0.438	
11	70.00	Et ₃ SiH	2.20	5.22	0.200	0.148	
12	70.00	Et ₃ SiH	2.60	6.64	0.151	0.073	
13	80.05	Et ₃ SiH	1.76	3.94	0.270	0.292	1.3 - 2.7
14	80.05	Et ₃ SiH	2.06	4.79	0.217	0.148	
15	80.05	Et ₃ SiH	2.06	4.79	0.217	0.073	
16	80.05	Et ₃ SiH	2.31	5.58	0.186	0.037	
2	80.05	none	2.16	5.11	0.204	0.0	
24	70.00	none	2.87	7.54	0.138	0.0	
25	70.00	none	2.87	7.54	0.138	0.0	

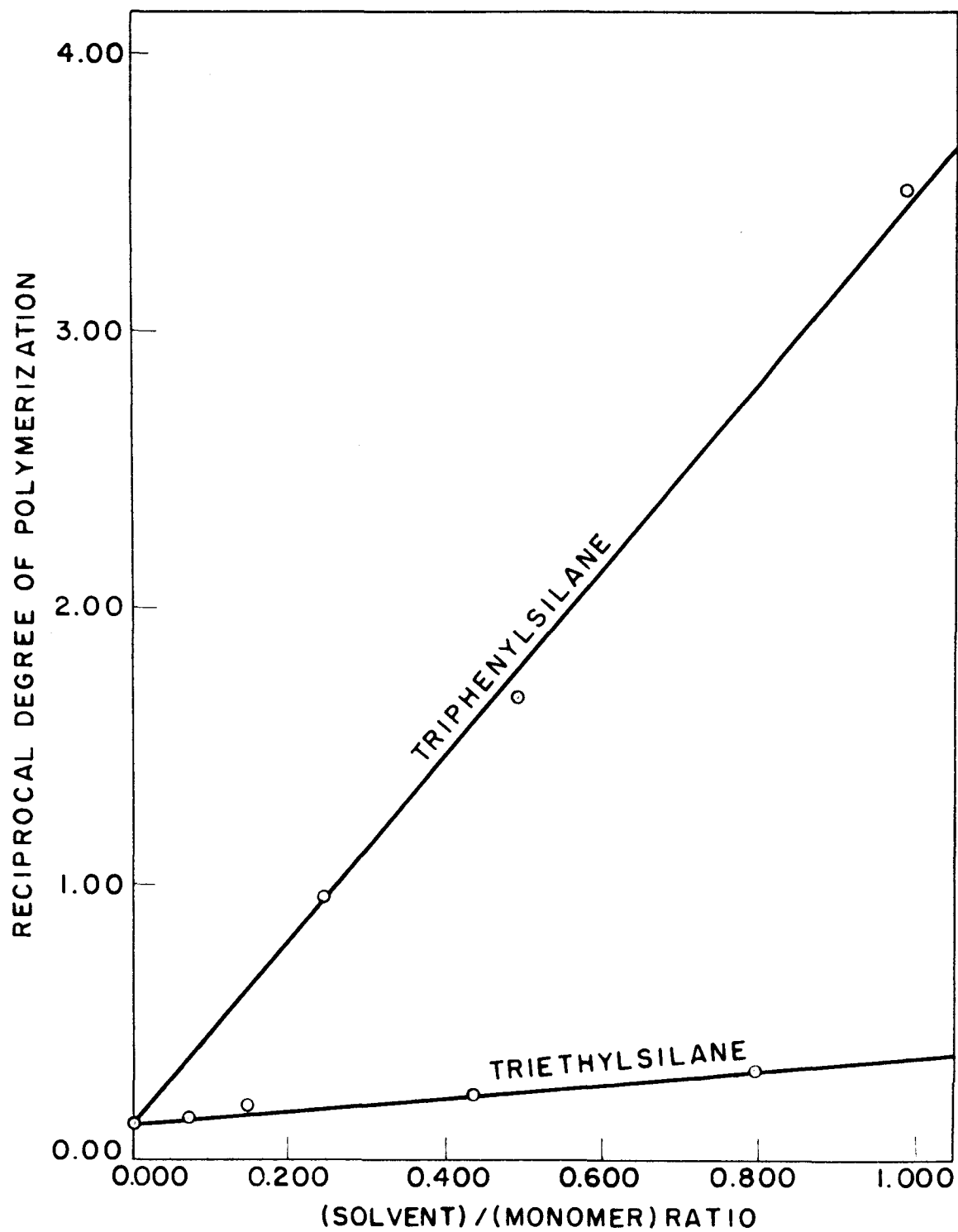


Figure 1

Chain Transfer Constants of Triphenylsilane
and Triethylsilane at 70°

Radical Induced Reactions of Triphenylsilane

Reaction of triphenylsilane, oxygen and benzoyl peroxide in benzene. Into a 500 ml. three-necked round-bottomed flask equipped with a blade stirrer, a condenser and a gas inlet tube leading to the bottom of the flask, there was introduced a solution of 36.0 g. (0.138 mole) of triphenylsilane and 1.00 g. (0.0045 mole) of benzoyl peroxide dissolved in 170 ml. dry benzene. The flask was heated to a temperature of 95° (bath temperature), while oxygen was bubbled in through the inlet tube and vigorous stirring was maintained. The reaction was continued for 9 hours. The benzene was removed by distillation at reduced pressure. The temperature of the residual solution did not exceed 30°. When the volume of the residue was reduced to about 75 ml., 12.21 g. of white crystals was deposited. These crystals (m.p. 152-154°) gave no depression of the melting point of an authentic specimen of triphenylsilanol in the determination of the m.p. of a mixture of the two. Further evaporation of the solvent led to the recovery of two more crops of 0.51 g. and 4.33 g. of crystals melting at 148-149° and 136-139° respectively. An infrared spectrum of the latter fraction showed bonds due to both triphenylsilanol and triphenylsilane. The residual solution (about 25 ml.) was diluted with petroleum ether (b.p. 60-70°) and

chilled to deposit further crops of crystals. Repeated crystallization of these latter oily crystals from petroleum ether (b.p. 60-70°) yielded three crops of crystals weighing 6.40 g., 3.78 g., and 0.94 g. respectively; with m.p.'s of 42-44°, 39-45° (recrystallized, 43-45°), and 44-46°. These low melting crystals gave a positive silicon-hydrogen bond test⁵¹ (formation of gas upon treatment with methanolic KOH), and they were presumed to be triphenylsilane. The red oily residue resisted attempts at crystallization. The total triphenylsilanol isolated amounted to 44.8 per cent of the initial triphenylsilane, and a total of 28.2 per cent of triphenylsilane was removed.

A similar experiment at lower temperatures (58-60°) resulted in no apparent reaction. Only triphenylsilane was recovered (88 per cent) and no evidence of oxygenated products presented itself.

A control run was made under the conditions of the initial oxidation, without the addition of benzoyl peroxide. The same work-up procedure resulted in a 77 per cent recovery of triphenylsilane, and no other products were noted.

Rates of oxidation of triphenylsilane. The rates of oxidation of triphenylsilane were measured by following the

⁵¹F. S. Kipping, J. Chem. Soc., 119, 848 (1921).

oxygen uptake. The apparatus (designed and generously lent by Dr. C. E. Boozer of these laboratories) consisted of gas burets thermostatted at 25.00° , connected to a reaction cell which could be maintained at either 62.5° or 74.4° . The cell was equipped with a magnetic stirrer. An automatic levelling device consisting of a mercury pressure reservoir manostat with contacts leading to a relay-operated oxalic acid solution electrolysis cell provided a means for following the oxidations smoothly and with little lag. This apparatus was adapted from one designed by Bolland⁵². The apparatus was evacuated and flushed several times with oxygen before each run. Azo-bis-isobutyronitrile was used as the initiator in each experiment.

Three runs were made, one at 62.5° and two at 74.4° . Table 5 summarizes the experimental conditions for each run. Table 6 includes the data collected for the second run, and Figure 2 shows a plot of the logarithm of the per cent remaining triphenylsilane (in which the remaining triphenylsilane is calculated as initial moles triphenylsilane less moles of oxygen absorbed) against time for the three runs. In each run, an increasing deviation from first order kinetics appears as the reaction progresses.

⁵²J. L. Bolland, Proc. Roy. Soc., A186, 218 (1946).

Table 5
Oxidations of Triphenylsilane

Run no.	Triphenylsilane initial conc. (moles/liter)	Initiator ^a conc. (moles/liter)	Cell temp. (°C)	Barometric pressure ^b (mm. Hg)
1	1.280	0.101	62.5	742.77
2	1.280	0.101	74.4	736.98
3	2.560	0.101	74.4	732.54

^aAzo-bis-isobutyronitrile was used as the initiator in each case.

^bPressures were corrected for difference of expansion of mercury and the brass scale.

Two 1.00 ml. aliquots of the reaction mixture of run 1 were titrated iodometrically with 0.0500 N sodium thiosulfate; the first, acidified with acetic acid only, required 6×10^{-3} meq. of thiosulfate; the second, acidified with hydrochloric acid and heated for a short time, required 0.17 meq. of the thiosulfate solution. The total oxygen absorbed was 0.201 meq., thus, the total reducible material in the solution amounts to 85 per cent of the oxygen absorbed, if this reducible material is present as peroxides.

Reaction of triphenylsilane and di-tert-butyl peroxide in chlorobenzene. In a 1 l. round-bottomed flask fitted

Table 6

Oxidation Rate of Triphenylsilane at 74.4° (Run 2)

Time (run)	Volume oxygen absorbed (ml.)	Moles oxygen absorbed $\times 10^4$	Log per cent remaining triphenylsilane
5.00	1.09 ^a	0.432	1.9981
10.00	1.82	0.721	1.9959
15.00	2.48	0.983	1.9944
20.00	3.05	1.209	1.9931
25.00	3.58	1.419	1.9919
35.00	4.46	1.770	1.9899
50.00	5.53	2.192	1.9874
60.00	6.07	2.410	1.9862
70.00	6.70	2.655	1.9847
85.00	7.42	2.942	1.9830
100.00	8.05	3.190	1.9816
120.00	8.42	3.340	1.9806

^aThe initial volume of oxygen was determined by extrapolating the first few readings to zero time.

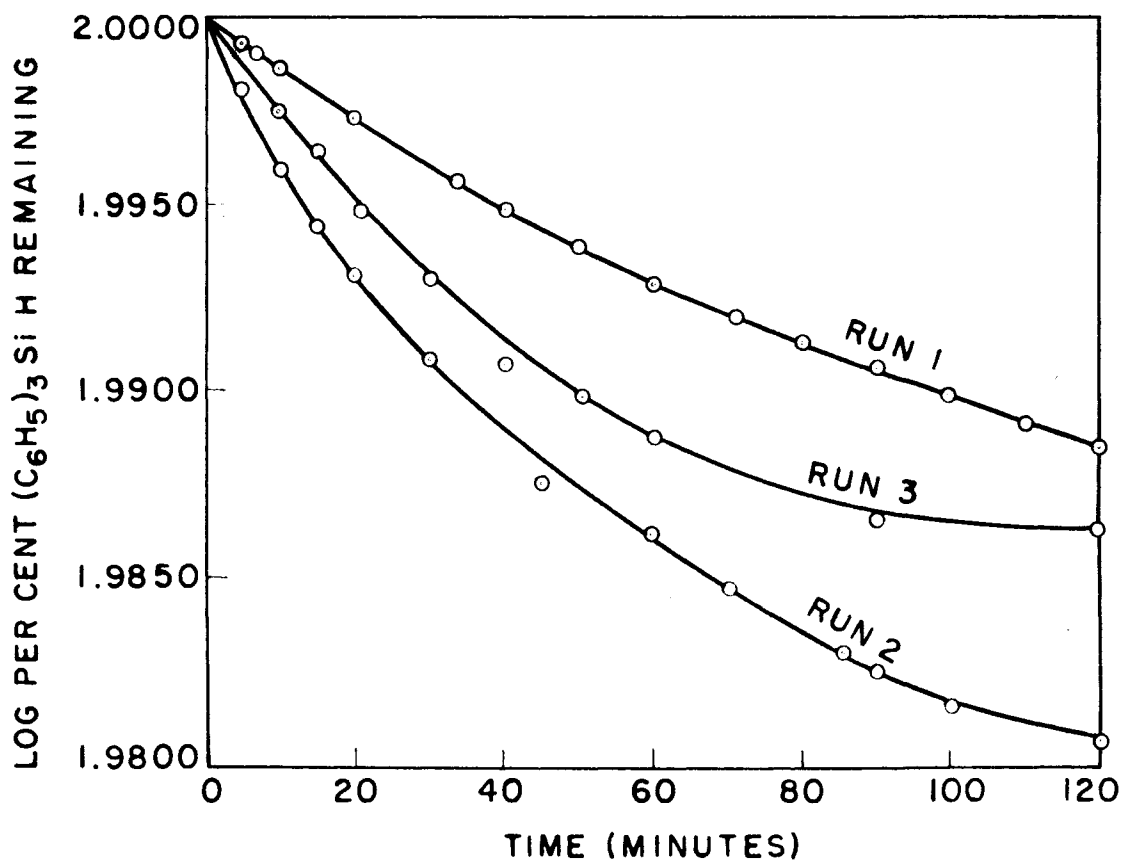


Figure 2

Rates of Oxidation of Triphenylsilane in
Chlorobenzene at 62.5 and 74.4°

with a reflux condenser, a nitrogen inlet tube leading to the bottom of the flask, and a thermometer was placed 70.0 g. of triphenylsilane (0.269 mole), 79.4 g. di-tert-butyl peroxide (0.544 mole) and 215 ml. of chlorobenzene. The mixture was heated to reflux, and refluxed for 31 hours. The temperature varied from 122 to 103° as volatile products formed. The chlorobenzene and volatile products were removed by distillation through a 1 m. helix packed column, and vacuum distilled to yield a liquid product (b.p. 89-95° at 0.4 mm.) and several fractions boiling from 145-173° at 0.5 mm. which solidified on cooling. One of these fractions (b.p. 158-161° at 0.5 mm.) was crystallized from benzene, yielding 15.8 g. of near white crystals, m.p. 89-93°. Recrystallization of this material from petroleum ether (b.p. 60-90°) yielded 12.9 g. of white crystals melting at 94-95.5°. A mixture of this material with an equal amount of authentic triphenylchlorosilane (m.p. 94-95°) melted at 94-95.5°. A portion of the material melting at 94-95.5° was hydrolyzed by shaking it in ether solution with an equal volume of 5 per cent aqueous sodium hydroxide solution, and, upon acidification (with nitric acid) gave a white precipitate with silver nitrate solution. The precipitate was soluble in dilute ammonia and could be reprecipitated by acidification with nitric acid. The crude yield of

triphenylchlorosilane (material melting at 89-93°) amounted to 20 per cent of the theoretical. The residue, a black tarry mass, could not be induced to crystallize. The liquid product was not identified in this experiment.

Another similar run was made with smaller quantities, using the same general set-up. Twenty-five ml. of di-tert-butyl peroxide (0.136 mole) and 30.0 g. (0.115 mole) of triphenylsilane were dissolved in enough chlorobenzene to make 250 ml. of solution; the solution was refluxed for 5 hours at temperatures ranging from 130-125°. The reaction mixture was assayed for triphenylsilane and triphenylchlorosilane by method described in the section immediately following this one. The triphenylsilane remaining unreacted was determined as 23.3, 23.3 and 24.1 per cent of the initial charge in triplicate determinations. Triphenylchlorosilane was assayed as 36.5 and 36.6 per cent of the theoretical yield, based on triphenylsilane.

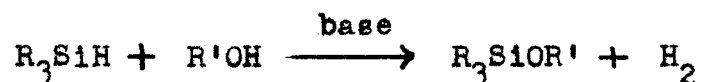
The chlorobenzene, unreacted peroxide and volatile products were removed by distillation at reduced pressure. The residue was distilled through a 12 inch unpacked externally heated column at pressures of 0.01-0.06 mm. An initial fraction (b.p. 65-111° at 0.06 mm., weight 0.74 g.) was collected. An infrared spectrum of a portion of this sample dissolved in carbon disulfide showed major peaks

(per cent transmittance less than 80 for a solution in which the most intense peak shows a per cent transmittance of 5) at wave lengths of 3.28, 8.00 (double peak), 8.90, 9.16, 9.32, 9.63, 10.67, 12.07, 12.70, 13.2-13.4 (broad), 14.4 and 14.7 microns. Purified samples of o-chlorobiphenyl and p-chlorobiphenyl were examined spectroscopically by the same method. The ortho isomer showed major peaks at 3.25, 8.00 (double peak), 8.90, 9.32, 9.64, 9.94, 10.68, 13.40, and 14.75 microns. The para compound had major peaks at 3.25, 9.18, 12.09, 13.20, and 14.45 microns. Examination of the wave-lengths of the peaks reveals that all major peaks of both o-chlorobiphenyl and p-chlorobiphenyl are present in the spectrum of the liquid product, and that no major peak present in the liquid product fails to be present in the spectrum of either o-chlorobiphenyl or p-chlorobiphenyl, with the single exception of the 12.70 micron peak of the mixture which is present in neither of the spectra of pure compounds. The general shape of the peaks and the fine structure of the spectra are also consistent with the hypothesis that the liquid product is a fairly pure mixture of o-chlorobiphenyl and p-chlorobiphenyl. Some attempts at separation of the isomers were made, but crystallization, chromatography and sublimation with this and product mixtures from similar experiments failed to resolve the small amounts of "liquid fractions" collected.

A subsequent fraction (b.p. 125-160° at 0.01 mm.) solidified on cooling, yielding 12.7 g. of white, oily crystals melting at 75-90°. Crystallization of this material from petroleum ether (b.p. 60-90°) gave 7.58 g. of crystals melting at 89-93.5°. Recrystallization raised the melting point to 95-97°, and this melting point was not depressed by mixing the purified material with purified authentic triphenylchlorosilane. The yield of the triphenylchlorosilane isolated as material melting at 89-93° was 22.0 per cent.

A similar run, using the same concentrations of reactants, but in which the volatile products were allowed to escape through a 6 inch externally heated column attached to the reaction flask, was carried out for 21 hours at temperatures of 128-137°. The yield of triphenylchlorosilane, determined by titration as described in the following section, was 62.4 per cent.

Assay of triphenylsilane. Triphenylsilane was determined in the reaction mixture by measuring the volume of hydrogen evolved in the reaction with base⁵¹.



The determination was carried out in a Zerewitinoff apparatus. The gas buret and reaction cell were thermostatted at 25.00°;

potassium hydroxide in n-butyl alcohol was used as the reaction medium, and n-butyl alcohol was used as the retaining fluid to equalize the vapor pressure. A correction was applied for the vapor pressure of n-butyl alcohol at 25°. Determinations with 3 ml. aliquots of standard solutions of triphenylsilane in chlorobenzene gave results of 98.7-99.7 per cent of the triphenylsilane present. Triphenylchlorosilane was found not to interfere.

Assay of triphenylchlorosilane. Triphenylchlorosilane was found to solvolyze rapidly in 95 per cent ethanol to release hydrogen chloride which could be titrated with standard alkali to obtain values of 97.4-97.8 per cent of the theoretical for samples of Dow Corning (purified grade) triphenylchlorosilane crystallized once from petroleum ether (b.p. 60-90°).

Sealed tube reactions of triphenylsilane and di-tert-butyl peroxide in halobenzenes. The formation of triphenylhalosilanes from the peroxide initiated reaction of triphenylsilane in halobenzenes was studied further by means of the triphenylchlorosilane assay mentioned previously. Tubes made from pyrex 15 mm. o.d. tubing were filled to about one-third their volume with various reaction mixtures, degassed by alternate freezing and thawing under vacuum, and sealed under vacuum. The tubes were placed in an oil bath maintained at

135.0° and individual ampules withdrawn at various intervals. The tubes were cooled, broken, and the contents washed into a flask containing ethanol. The acid released was titrated with standard alkali, using brom-phenol-blue as an indicator. Table 7 summarizes the data thus collected. Each tube contained 7.00 ml. of solution.

A tube containing 2 ml. each of chlorobenzene and di-tert-butyl peroxide was heated at 135.0° for 25.5 hours, and titrated in the same manner. No acid was released (within experimental error estimated at 0.002 meq.), but a discoloration of the solution was noted.

Attempted Preparations of an Organosilicon Peroxide

Reaction of triphenylchlorosilane with sodium peroxide in benzene. Five grams (0.061 mole) of 95 per cent sodium peroxide was suspended in 50 ml. of dry benzene, by vigorous stirring with a single-blade stirrer. Five grams (0.017 mole) of Dow-Corning purified triphenylchlorosilane dissolved in 85 ml. dry benzene was added fairly rapidly. No evidence of reaction was noted during the addition, but the flask did become warm after stirring had been continued for 35 minutes. The reaction mixture was allowed to stand overnight, and then excess water was added to hydrolyse the remaining sodium

Table 7

Sealed Tube Reactions of Triphenylsilane with
Di-tert-butyl Peroxide at 135.0°

Tube	Moles $\text{Ph}_3\text{SiH} \times 10^3$ (initial)	Moles $\text{tBu}_2\text{O}_2 \times 10^3$ (initial)	Time (min.)	Meq. acid formed
1 ^a	3.84	2.72	30.0	0.359
2 ^a	3.84	2.72	79.0	0.758
3 ^a	3.84	2.72	134.0	1.142
4 ^a	3.84	2.72	205.0	1.33
5 ^a	3.84	2.72	509.0	1.52
6 ^a	3.84	2.72	1140.	1.58
7 ^a	1.92	2.72	1530.	0.372
8 ^a	0.384	2.72	1530.	0.043
9 ^a	0.384	0.544	1530.	0.115
10 ^a	0.384	0.109	1530.	0.063
11 ^b	3.84	2.88	1530.	0.148
12 ^c	3.84	2.72	1530.	1.00
13 ^{a, d}	3.84	2.72	1530.	0.002
14 ^{b, d}	3.84	2.72	1530.	0.01

^aChlorobenzene as solvent.

^bFluorobenzene as solvent.

^cBromobenzene as solvent.

^dOne gram (5.49×10^{-3} mole) of benzophenone added.

peroxide and triphenylchlorosilane. The benzene layer was washed twice with water and dried over sodium sulfate. Upon evaporation of the benzene, 4.09 g. of slightly oily cream colored crystals was left. This material (m.p. 141-150°) was crystallized from petroleum ether (b.p. 80-110°) to give 2.91 g. of white crystals, m.p. 152-153°. This material showed no depression of m.p. upon mixture with authentic triphenylsilanol. The recovery (crude) amounted to 86 per cent of the theoretical amount of triphenylsilanol. No other materials were isolated from the reaction.

Reaction of triphenylchlorosilane with aqueous sodium peroxide. Ten grams of 95 per cent sodium peroxide (0.128 mole) was added to 200 ml. of cold water with rapid stirring; evolution of gas was noted as the solid peroxide came into contact with water. Iodometric titration of samples of the peroxide solution showed that 67 per cent of the sodium peroxide added was present as peroxide, the rest having presumably been converted to sodium hydroxide. To this aqueous solution was added, with stirring, 34.1 g. (0.116 mole) of triphenylchlorosilane in 250 ml. of benzene. The reaction mixture was cooled in an ice bath during the addition, and stirred for one hour, after which the reaction mixture was allowed to come to room temperature. The benzene layer was removed, dried, concentrated, and finally, evaporated to

yield 30.6 g. of white crystals, m.p. 149-153°. This material showed no depression of m.p. upon mixture with authentic triphenylsilanol, m.p. 152-153.5°. A small quantity (0.17 g.) of material insoluble in either the benzene or water layer was filtered off and recrystallized from petroleum ether (b.p. 80-110°) to yield crystals melting at 233-236°. This material did not depress the m.p. of an authentic specimen of hexaphenyldisiloxane. The total yield of triphenylsilanol and hexaphenyldisiloxane amounted to 97 per cent of the theoretical, based on triphenylchlorosilane. No other products were isolated.

Infrared Absorption Spectra

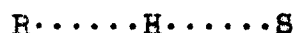
All infrared absorption spectra were measured with a Baird associates Infrared Recording Spectrophotometer (Model B). This instrument was made available through the generosity of the Institute for Atomic Research. The author wishes to express his appreciation to Dr. M. Margoshes and Mr. R. M. Hedges, who recorded the spectra and contributed helpful information to the problem of the interpretation of the spectra.

DISCUSSION

The question of possible resonance stabilization of a triphenylsilyl radical can be approached through the interpretation of the chain transfer constants of triphenylsilane and triethylsilane evaluated in Table 4. By arguments outlined in the Historical section of this Thesis, Mayo and co-workers³³⁻⁴¹ have correlated the chain transfer constants of a number of hydrocarbon solvents with the relative resonance stabilizations of the S· species formed in the chain transfer process.

From examination of Table 2 it can be seen that such a correlation is limited to processes involving the breaking of a carbon-hydrogen bond in the solvent, and that a statistical correction for the number of carbon-hydrogen bonds available sharpens the comparisons between the different types of carbon-hydrogen bonds examined. Benzene and aliphatic hydrogens possess low reactivity towards the growing polymer chain; benzylic hydrogens are markedly more active, increasingly so with increasing substitution. Tert-butylbenzene, which has no benzylic hydrogens available, drops to the level of reactivity of aliphatic compounds. Diphenylmethane and triphenylmethane show increasing activity in the order stated. However, these effects are small when they

are compared with the relative resonance energies of the S· species formed; the differences between the resonance energies of aliphatic and benzyl radicals, between benzyl and diphenylmethyl, and between diphenylmethyl and triphenylmethyl are all at least ten kcal./mole⁹. At 60°, a difference of ten kcal./mole in activation energies of two reactions with equal frequency factors corresponds to a factor of 3×10^6 in the rates; five kcal./mole would result in a 2×10^3 factor, and two kcal./mole, a factor of 20. Thus the energy of the transition state



is influenced by the reorganization energy of the S· species, but this transition state energy is not as sensitive to such a reorganization energy as would be the energy for a transition state for a process in which a radical were more completely formed.

Mayo and Gregg³⁵ have pointed out that for most of the solvents presented in Table 2, increasing chain transfer constants correlate with decreasing activation energies and increasing frequency factors, the former effect dominating the latter. Since the effect of stabilization of the S· species would be expected to influence only the activation

energy through weakening the carbon-hydrogen bond, the increase in frequency factor with more active solvents would also tend to decrease the sensitivity of the chain transfer reaction to the S· reorganization energy.

At 70°, the chain transfer constant of triphenylsilane is greater than that of triethylsilane by a factor of 13.7. At 80°, the ratio is more uncertain, but it probably lies between 14 and 28. These ratios point to a definitely lower free energy of activation for the triphenylsilane chain transfer process than for the triethylsilane transfer. The higher rate of the triphenylsilane transfer may be attributed to greater resonance stabilization of the triphenylsilyl radical with respect to the triethylsilyl radical; uncertainty as to the relative importance of the frequency factors and activation energies³⁵ of the process preclude any possibility of estimating a reliable value of the resonance stabilization of the triphenylsilyl radical.

The chain transfer constants of both the silanes tested show a high degree of reactivity relative to the hydrocarbon solvents in Table 2. The chain transfer constants of triethylsilane and triphenylsilane at 60° can be estimated from the 70° and 80° values given in Table 4 as 300×10^{-5} and 22×10^{-5} respectively; these values can then be compared directly with those of Gregg and Mayo in Table 2.

Triethylsilane lies between diphenylmethane and triphenylmethane, and triphenylsilane is a more efficient transfer agent than triphenylmethane, approaching carbon tetrachloride in reactivity. The silicon-hydrogen bond energy at 298°K has been calculated from critically evaluated data as 79 kcal/mole, while carbon-hydrogen bonds have an energy of 88 kcal/mole on the same scale⁵³. The lower silicon-hydrogen bond energy is most probably responsible for the increased efficiency of silicon-hydrogen compounds over hydrocarbons in the chain transfer reactions.

It was pointed out in the Historical section of this Thesis that the S· species must enter into the polymerization with high efficiency if the steady-state treatment can be applied to the solution of the kinetics of the chain transfer process. If the S· reactive centers were to destroy themselves by dimerization or bimolecular disproportionation, a lower value of the second order rate constant for the overall polymerization would be observed. The data of Gregg and Mayo³⁵ for the solvents presented in Table 2 show no such trend, even for those solvents which give high values for the chain transfer constants.

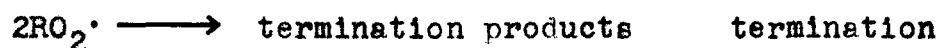
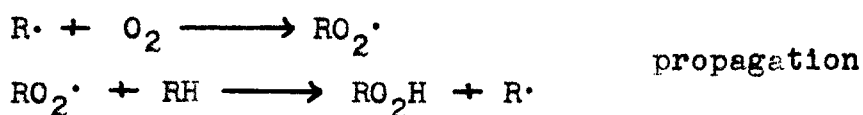
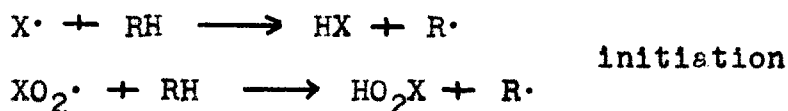
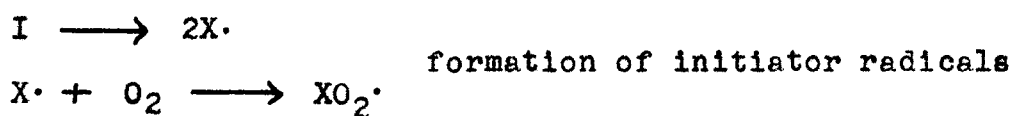
⁵³M. L. Huggins, J. Am. Chem. Soc., 75, 4124 (1953).

The data presented in Table 3 allow no precise calculation of the second order rate constants for the overall polymerization process, but, by assuming volume additivity of the silanes and styrene, the rate constants can be approximated from the per cent polymerization observed. These constants range from 2×10^{-4} to 11×10^{-4} liters mole⁻¹hour⁻¹ at 70°; at 80°, from 6×10^{-4} to 14×10^{-4} liters mole⁻¹hour⁻¹. No trend towards lower values of the second order rate constant for solutions containing higher concentrations of silanes is evident; in fact, at both 70° and 80°, the rate constants of the bulk sample were the smallest of those observed.

These values are in fair agreement with those of Gregg and Mayo³⁵, who obtained second order rate constants ranging from 0.85×10^{-4} to 2.63×10^{-4} liters mole⁻¹hour⁻¹ at 60°, and from 21×10^{-4} to 42×10^{-4} at 100°. It can be stated, then, that the data in Table 3 show no evidence for an "abnormal" radical-radical termination process, and that they preclude a large effect of this type.

The benzoyl peroxide induced oxidation of triphenylsilane is clearly a chain process, since a control run in which no peroxide was added shows no autoxidation under the same experimental conditions as those of the peroxide

initiated reaction, and since the benzoyl peroxide was present only in a small amount (0.032 mole per mole of triphenylsilane). A generally accepted formulation of the mechanism for radical induced liquid phase hydrocarbon oxidations at "low" temperatures (50-150°) may well apply here⁵⁴.

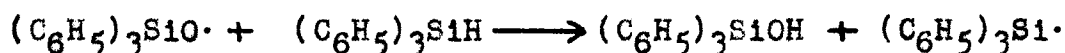
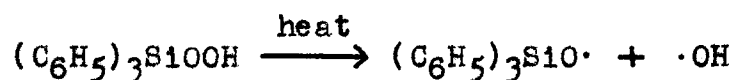


Hydroperoxides are the postulated initial products of the oxidation in the scheme given above, and they are indeed isolable products of many hydrocarbon oxidations, such as

⁵⁴E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, Disc. Faraday Soc., 10, 242 (1951).

the radical induced oxidations of isobutane^{55,56}, and tetralin⁵⁷.

The oxidation of triphenylsilane with benzoyl peroxide in benzene gave triphenylsilanol as a major product, and no species corresponding to a hydroperoxide or ditriphenylsilyl peroxide, the silicon analogue of trityl peroxide¹, was isolated. It seems reasonable that such a product might further react under the conditions of the oxidation, in such a manner as indicated below.



The triphenylsilanol produced can thus be accounted for. No products illuminating the fate of the OH radical were isolated. Another proposed reaction, in which the triphenylsilyl radical attacks the hydroperoxide initially formed, is given below.

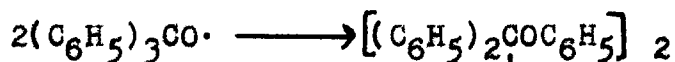
⁵⁵W. E. Vaughan and F. F. Rust, U. S. Patent 2,395,523 (C. A., 40, 3641 (1946)).

⁵⁶W. E. Vaughan and F. F. Rust, U. S. Patent 2,403,771 (C. A., 40, 5757 (1946)).

⁵⁷M. Hartmann and M. Seiberth, Helv. chim. Acta, 15, 1390 (1932).



If these reactions are correctly postulated, it is interesting to note that the triphenylsiloxy radical undergoes neither the disproportionation reaction characteristic of alkoxy radicals⁵⁸, nor the rearrangement associated with tritoxo radicals⁵⁹.



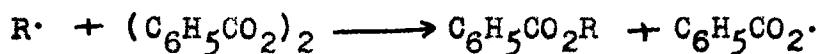
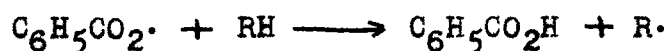
At sufficiently high oxygen pressures, the rate of radical initiated oxidation of moderately labile hydrocarbons is generally first order with respect to the hydrocarbon⁶⁰. This observed order is in agreement with rate expressions derived from the oxidation chain scheme given previously⁵⁴.

⁵⁸N. A. Milas and D. M. Surgenor, J. Am. Chem. Soc., **68**, 205 (1946).

⁵⁹H. Wieland, Ber., **44**, 2550 (1911).

⁶⁰L. Bateman, G. Gee, A. L. Morris and W. F. Watson, Disc. Faraday Soc., **10**, 250 (1950).

The oxidation of triphenylsilane does not obey the first order law under the conditions studied (see Figure 2), but falls off from first order as the reaction progresses; the deviation is more emphatic with increased temperature, and with increased concentration of the silane. These observations are consistent with the hypothesis of the formation of an inhibitor as the reaction progresses; such a hypothesis would lead to the conclusion that oxygenated products, such as triphenylsilanol or triphenylsilylhydroperoxide, could act as traps for the triphenylsilyl radicals. Such a sensitivity towards oxygenated compounds is not a common characteristic of hydrocarbon free radicals, although Cass⁶¹ has postulated such a reaction to explain the rapid decomposition of benzoyl peroxide in ether solvents. Products isolated from



these reactions support such a postulate. However, carbon free radicals show no such reactivity towards the majority

⁶¹W. E. Cass, J. Am. Chem. Soc., 69, 500 (1947).

of oxygen containing compounds, and this property seems to be a characteristic one of silicon radicals, as evidenced by the oxidation studies and other observations discussed subsequently. The inhibition begins to make itself evident at rather low conversions of triphenylsilane, causing a strong deviation from a straight line first order plot at conversions of less than 5 per cent.

The identification of triphenylchlorosilane as a product of the reaction between di-tert-butyl peroxide and triphenylsilane in chlorobenzene shows another contrast between the behavior of triphenylsilyl radicals and hydrocarbon radicals. Chlorobenzene is generally inert towards most free radicals, serving as a solvent for radical reactions such as oxidation and the thermal decomposition of peroxides⁵⁴. Phenyl radicals produced by the decomposition of benzoyl peroxide do, however, attack chlorobenzene to form isomeric biphenyls^{62,63}. The abstraction of a chlorine atom from a benzene ring is nevertheless an unprecedented mode of reactivity for free radicals. It should be mentioned that Kapur⁶⁴ proposes a chlorine abstraction in the chain transfer reaction of styrene with

⁶²D. H. Hey, J. Chem. Soc., 1974 (1952).

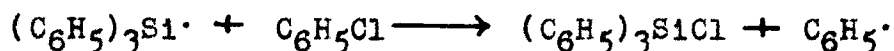
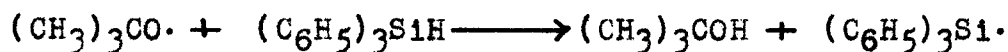
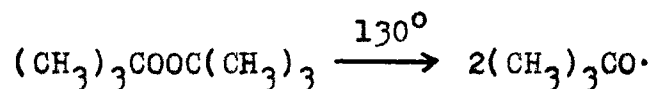
⁶³R. L. Dannley, E. G. Gregg, R. E. Phelps and C. B. Coleman, J. Am. Chem. Soc., 76, 445 (1954).

⁶⁴S. L. Kapur, J. Polym. Sci., 11, 399 (1953).

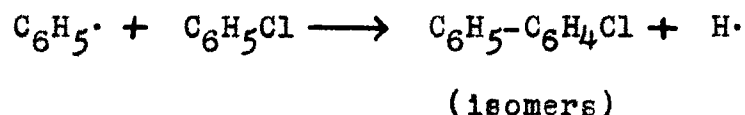
chlorobenzene. His data, however, do not require or support such a hypothesis.

In an investigation of the chain transfer of styrene radicals with bromobenzene, Mayo⁴⁰ found that no bromine was incorporated in the polystyrene; an earlier report by Breitenbach⁶⁵ gave similar results for chlorobenzene. These observations conflict with Kapur's⁶⁴ chlorine abstraction hypothesis, and led Mayo to propose a mechanism for chain transfer of styrene with benzene, chlorobenzene and bromobenzene involving the formation of a radical complex with the aromatic solvent, and the subsequent reaction of the complex with a styrene molecule to transfer the reactive center.

The formation of triphenylchlorosilane suggests the following reaction scheme for the triphenylsilane-di-tert-butyl peroxide-chlorobenzene system.



⁶⁵J. W. Breitenbach, Naturwissenschaften, 29, 708, 784 (1941).



The observed formation of a mixture of monochlorobiphenyls (ortho and para isomers) lends support to such a scheme, and agrees with the observations of Hey⁶² relevant to the reaction of phenyl radicals with chlorobenzene.

The removal of the volatile products of the peroxide decomposition (acetone and tert-butyl alcohol) as they are formed increases the yield of triphenylchlorosilane. This observation suggests a competition of the volatile products with chlorobenzene for the attentions of the triphenylsilyl radical. Such a competition correlates with the sensitivity of triphenylsilyl radical towards oxygenated products which was invoked to explain the results of the oxidation rate experiments with triphenylsilane.

The sealed tube experiments presented in Table 7 further elucidate this reaction. The first order rate constant for the decomposition of di-tert-butyl peroxide at 135° has been determined in several solvents at values ranging from 3.6-5.2 x 10⁻⁵ sec⁻¹.⁶⁶ If the scheme presented above or on the previous page properly represents the reaction, and

⁶⁶J. A. Raley, F. F. Rust and W. E. Vaughan, J. Am. Chem. Soc., 70, 1336 (1948).

there is no chain reaction induced by the hydrogen atom or other terminal species, the rate of formation of triphenylsilane would be expected to follow the rate of decomposition of the peroxide. Since each molecule of peroxide produces two molecules of the peroxy radical, the highest rate of formation of triphenylchlorosilane that can be expected is simply twice that of the peroxide decomposition. Any reduction in the efficiency of the chlorine abstraction process by reaction of triphenylsilyl radicals with competing substrates would cause the rate of formation of the triphenylchlorosilane to fall off. In the experiments listed in Table 7, tubes 1 to 6, containing identical reagent mixtures, were heated at 135.0° for varying lengths of time. Fictitious first order rate constants were calculated for each tube, calculated from the formula given below.

$$k_1 = \frac{1}{t} \log e \frac{[(C_6H_5)_3SiH]_0}{[(C_6H_5)_3SiH]_0 - [(C_6H_5)_3SiCl]}$$

Table 8 shows the results of these calculations.

The accelerating deviation from first order kinetics again suggests a competition of the oxygen containing products for the triphenylsilyl radical. The introduction of benzophenone in tube 18 reduced the formation of

Table 8

Rates of Formation of Triphenylchlorosilane

Tube no.	Time (sec.)	$k_1 \times 10^5$ (sec. ⁻¹)
1	1800	5.38
2	4740	4.66
3	8050	4.36
4	12300	3.48
5	30500	1.65
6	68400	0.77

triphenylchlorosilane to zero. This observation supports the same contention.

The formation of acid-releasing material in the sealed tube reactions in which bromobenzene and fluorobenzene were used as solvents indicates the participation of these halobenzenes in the halogen abstraction reaction. Bromobenzene appears to be quite active in this respect, forming 25 per cent of the theoretical quantity of acid-releasing material, as compared with 40 per cent for the same reaction carried out in chlorobenzene. Fluorobenzene forms acid to the

extent of 4 per cent of the theoretical, a small but definite effect.

Further examination of Table 7 (tubes 6-10) shows that the yield of triphenylchlorosilane falls off if the amount of peroxide is either decreased far below the equivalent amount of triphenylsilane, or increased far above it. The former effect precludes a chain reaction of any efficiency, and the latter suggests again the competition of the peroxide decomposition products for the triphenylsilyl radical.

Two examples of attempts at the preparation of a triphenylsilylhydroperoxide or peroxide are included in the Experimental section. The isolation of triphenylsilanol in each case indicates that triphenylchlorosilane has greater sensitivity to nucleophilic attack by the hydroxyl ion present than to the hydroperoxyl ion under the conditions studied.

The halogen abstraction reactions exhibited by the triphenylsilyl radical are unusual in that they involve the breaking of the aromatic carbon to halogen bond, and the formation of a phenyl radical, a species with a high energy level and little reorganization energy⁹. The high value of the silicon-halogen bond energies (135, 90 and 73 kcal/mole for the bonds involving fluorine, chlorine and bromine respectively) given by Huggins⁵³ suggest that the transition

states for the halogen abstraction reactions reflect a considerable silicon-halogen bond formation. The silicon oxygen bond energy, 101 kcal/mole on the same scale suggests a similar explanation for the sensitivity of the triphenylsilyl radical towards oxygen containing compounds.

The absence of hexaphenyldisilane, the product which would arise from the dimerization of triphenylsilyl radicals, from all the product mixtures involving reactions of these radicals points to a high degree of reactivity for this species, and it appears that the earlier attempts to isolate a triphenylsilyl radical as a stable species at ordinary temperatures were doomed to failure. It should be pointed out that the detection of hexaphenyldisilane in almost any reaction product mixture is an easy task, since this compound is highly insoluble in the common organic solvents.

SUMMARY

Organosilicon free radicals have been studied by various means as an intermediate in several types of reactions.

The chain transfer constants of triphenylsilane and triethylsilane in the polymerization of styrene were determined. These silanes were found to have a relatively high aptitude for chain transfer.

A novel chlorine abstraction by the triphenylsilyl radical was discovered in the reaction of di-tert-butyl peroxide, triphenylsilane and chlorobenzene. A rate study was carried out on this reaction, and the scope extended to include other halobenzenes.

The radical induced oxidation of triphenylsilane to triphenylsilanol was demonstrated, and rate measurements of the process carried out by measuring the rate of oxygen uptake.

Organosilicon free radicals studied in these processes were found to be highly reactive, and to be especially sensitive towards electronegative groups. The chain transfer reactivity of triphenylsilane and triethylsilane, and the reactivities of the triphenylsilyl radical in the processes listed above were found to correlate qualitatively with the energies of the bonds broken and formed in the processes.

ACKNOWLEDGMENTS

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