The rate of hydrolysis varies somewhat with ionic strength of the buffer. This is shown by the following data on the hydrolysis of methyl benzylidenepyruvate in three phosphate buffers, all of *p*H 7.72 and 11.8% in methanol.

Soln. A Na_2HPO_4, mole/l.	Soln. B KH_2PO_4, mole/l.	Ionic strength, μ	$k' \times 10^3$, sec.$^{-1}$
0.2	0.6	0.6	2.23
.15	.45	.45	2.06
.1	.3	.3	1.77

This relationship is not quite linear. Ionic strength was calculated from the expression $\mu = {}^1/_2 cz^2$ in which c is the concentration in moles per liter and z is the ionic charge. These results are subject to some uncertainty due to varying liquid junction potentials at different ionic strengths.

Kinetic Measurements.—A Beckman DU spectrophotometer was provided with four Beckman thermospacers through which water at 25 ± 0.1° was circulated from a thermostat, thus maintaining the cell compartment at 24.8 ± 0.1°. In the summer the room temperature was kept close to 25° by means of an air conditioner. For the higher temperature the thermostat was held at 35 ± 0.2° and the cell temperature was 34.6 ± 0.2°.

Spectra were taken of 4×10^{-5} *M* solutions of acid in the alkaline hydrolysis buffer (where it exists as the anion) and the same concentration of ester in a buffer of *p*H 4 (0.2 *M* potassium dihydrogen phosphate–phosphoric acid). This weakly acidic buffer prevents any alkaline hydrolysis of the ester. From the plot of these spectra a wave length was then chosen where there was a difference of 0.2–0.4 absorbancy (optical density) unit and where the readings were in the more accurate part of the absorbancy scale (0.75–0). If the slope of the absorption curve of the acid anion is a minimum or is changing slowly, a more precise end-point can be reached (A_∞). Figure 2 shows spectra for benzylidenepyruvic acid and its methyl ester. Rates for this ester were measured at 345 mμ and a narrow slit width, 0.25 mm. Experiment showed that both acid and ester solutions followed Beer's law on dilution.

For the hydrolysis a methanol solution of the ester was added to the buffer in such a way as to minimize the temperature rise accompanying the addition of methanol (0.8° for 2 ml.). The ester solution was prepared from 2 or 4×10^{-4} mole dissolved in 50 ml. of purified methanol. In a stoppered 250-ml. erlenmeyer flask, 100 ml. of buffer and 1 ml. of methanol were brought to 24.5°. Then 1 ± 0.05 ml. of ester solution was dropped rapidly into the swirling buffer from a Mohr pipet with widened end, and a stop watch was started at the same time. As it does not enter the calculations, the exact concentration of ester is not critical and is determined by convenience. A 10-mm. stoppered, Beckman silica cell was filled as rapidly as possible, and the absorption was measured against the solvent cell filled with the same buffer. Readings were taken at 0.5 minute intervals at the start, later at longer intervals to determine the end value, A_∞. The solution in the cell came to constant temperature in about two minutes.

Values of log ($A - A_\infty$) were plotted against time. The table lists typical data for the hydrolysis of methyl *p*-methylbenzylidenepyruvate and the slope of the line multiplied by 2.303 is equal to k' (see equation 5).

Time, min.	A	$A - A_\infty$	Time, min.	A	$A - A_\infty$
1.5	0.410	0.340	5.0	0.305	0.235
2.0	.395	.325	6.0	.281	.211
2.5	.376	.306	7.0	.261	.191
3.0	.361	.291	8.0	.242	.172
3.5	.345	.275	9.0	.225	.155
4.0	.331	.261	10.0	.209	.139
4.5	.317	.247	54.0	.070	.0

The rate obtained in this way is 0.108 min.$^{-1}$. The best line was drawn through the first nine points with a very good fit (standard deviation from k' = 0.003). Based on the first 14 points representing 89% hydrolysis the standard deviation is 0.008. From six to nine determinations were made on each of the benzylidenepyruvic esters and four determinations on each benzoic ester. After hydrolysis the *p*H of each rate solution was measured. An occasional check of the complete spectrum of the hydrolysis solution indicated that no decomposition had taken place.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

A Study of Organosilicon Free Radicals

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Organosilicon free radicals have been studied as reactive intermediates in radical induced reactions of triphenylsilane, and as chain transfer agents in the thermal polymerization of styrene. Triphenylsilane was found to undergo a peroxide initiated oxidation to triphenylsilanol. The rates of oxidation of triphenylsilane initiated by azo-bis-isobutyronitrile were measured by following oxygen uptake. Evidence was found for the abstraction of chlorine from chlorobenzene by the triphenylsilyl radical; this reaction was studied under a variety of conditions.

Hexaaryldisilanes do not show any of the "unsaturated" properties characteristic of hexaphenylethane, nor do they show any other evidence of dissociation into triarylsilyl radicals at temperatures up to 130°.[2,3] The apparently higher bond dissociation energy of the Si–Si bond in a hexaaryldisilane, as compared to the C–C bond in a hexaarylethane, has been attributed to the lower reorganization energy of the triarylsilyl radicals, which can in turn be attributed to the lack of resonance energy of the triarylsilyl radicals, and the lack of steric strain in the hexaaryldisilane.[3a]

Following the procedures developed by Kharasch and co-workers for the addition of chloroform, carbon tetrachloride, and a wide variety of other reagents to the double bond of terminal olefins,[4] a

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(1) Du Pont Predoctoral Fellow 1952–1953.

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

(3) (a) H. Gilman and G. E. Dunn, THIS JOURNAL, **73**, 5077 (1951); (b) H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

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

number of workers[5] have effected peroxide or ultraviolet light initiated addition of various compounds containing an Si–H bond to a variety of compounds containing carbon–carbon double or triple bonds. This addition can best be explained as a free radical chain reaction of the type elucidated by Kharasch,[4] in which a silyl radical, formed by hydrogen abstraction[3] acts as the intermediate chain carrying species.

In the present study, triphenylsilyl radicals, produced by the action of peroxides or azo-bis-isobutyronitrile on triphenylsilane, were found to react with oxygen and, in the absence of oxygen, with chlorobenzene and other halogenated benzenes. The rates of these reactions were followed, and the products characterized. The hydrogen abstraction process was studied by determining the chain transfer constants of triphenylsilane and triethylsilane as solvents in the thermal polymerization of styrene. The methods developed by Mayo and his associates[6,7] were used for these determinations.

Experimental

Materials.—Triphenylsilane and triethylsilane were prepared by methods previously described.[8,9]

Chlorobenzene (Matheson Chemical Co.) was distilled through a 1-meter helix-packed column. Some batches were distilled through a 1.5-meter bubble-cap solvent column.

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

Styrene (Eastman Kodak Co. white label "stabilized") was washed several times with 5% 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 was 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.

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. of dry benzene. The flask was heated to a temperature of 95° for 9 hours while oxygen was bubbled in through the inlet tube and vigorous stirring was maintained. The benzene was removed by distillation at reduced pressure. Crystallization of the residue yielded 44.8% of triphenylsilanol, identified by mixed m.p. with an authentic specimen. From the same residue 22.8% of triphenylsilane was recovered and identified by a positive silicon–hydrogen bond test[10] and infrared spectrum. The balance of the material was a red oily residue which resisted crystallization.

A similar experiment carried out at 58–60° resulted in no apparent reaction. Only triphenylsilane was recovered (88%) and no evidence for the presence 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% 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 oxygen uptake. The apparatus (designed and generously lent by Dr. C. E. Boozer) was adapted from that of Bolland.[11]

Three runs were made, one at 62.5° and two at 74.4°. Table I summarizes the experimental conditions for each run. Figure 1 shows a plot of the logarithm of the percentage 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.

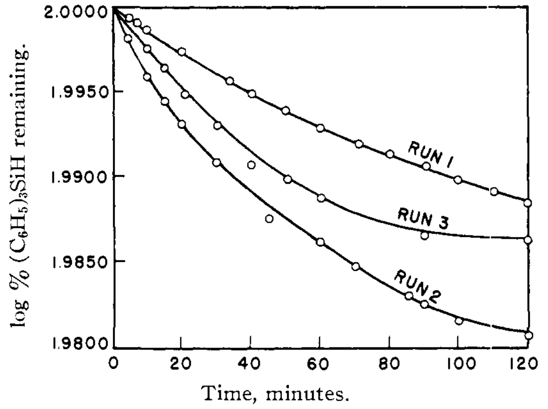

Fig. 1.—Rates of oxidation of triphenylsilane; azo-bis-isobutyronitrile, 0.101 *M* in all runs: run 1, silane 1.28 *M*, *T* 62.5°; run 2, silane 1.28 *M*, *T* 74.4°; run 3, silane 2.56 *M*, *T* 74.4°.

TABLE I

OXIDATION OF TRIPHENYLSILANE

Run	Triphenylsilane initial concn. mole/liter	Initiator[a] concn., mole/liter	Cell temp., °C.	Barometric[b] pressure, mm.
1	1.280	0.101	62.5	742.7
2	1.280	.101	74.4	736.9
3	2.560	.101	74.4	732.5

[a] Azo-bis-isobutyronitrile was used as the initiator in each case. [b] Pressures 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 0.27 meq. of the thiosulfate solution. The total oxygen absorbed was 0.201 meq.

Reaction of Triphenylsilane and Di-*t*-butyl Peroxide in Chlorobenzene.—In a one-l. round-bottomed flask fitted 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-*t*-butyl peroxide (0.544 mole) and 215 ml. of chlorobenzene. The mixture was heated at reflux 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

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(5) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **69**, 188 (1947); E. W. Pietrusza, L. H. Sommer and F. C Whitmore, *ibid.*, **70**, 484 (1947); C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947); R. Calas and E. Frainnet, *Bull. soc. chim. France*, 241 (1952); N. Duffant and R. Calas, *ibid.*, 241 (1952); R. Calas and N. Duffant, *ibid.*, 792 (1953); E. Frainnet, *ibid.*, 792 (1953); R. Calas, E. Frainnet and J. Valade, *ibid.*, 792 (1953); R. H. Krieble, U. S. Patent 2,510,642 [*C. A.*, **44**, 9473 (1950)]; L. O. Goldblatt and D. M. Oldroyd, U. S. Patent 2,533,240 [*C. A.*, **45**, 2262 (1952)]; C. A. Burkhard, THIS JOURNAL, **72**, 1402 (1950); British Thompson-Houston Co., British Patent 663,740 [*C. A.*, **46**, 11,228 (1952)] British Patent 661,094 [*C. A.*, **46**, 5365 (1952)]; G. N. Gadsby, *Research* (*London*), **3**, 338 (1950); H. Merten and H. Gilman, THIS JOURNAL, **76**, 5798 (1954).

(6) F. R. Mayo, *ibid.*, **65**, 2324 (1943); R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

(7) F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

(8) H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

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

(10) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 848 (1921).

(11) J. L. Bolland, *Proc. Roy. Soc.* (*London*), **A186**, 218 (1946).

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 pure triphenylchlorosilane melting at 94–95.5°, m.m.p. with authentic triphenylchlorosilane 95–95.5°. The crude yield of triphenylchlorosilane (material melting at 89–93°) amounted to 20% 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. Twenty-five ml. of di-*t*-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 five hours at temperatures ranging from 130–125°. The reaction mixture was assayed for triphenylsilane and triphenylchlorosilane by methods described below. The unreacted triphenylsilane was determined as 23.3, 23.3 and 24.1% of the initial charge in triplicate determinations. Triphenylchlorosilane was assayed as 36.5 and 36.6% 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 (percentage transmittance less than 80 for a solution in which the most intense peak shows a percentage transmittance of 5) at wave lengths of 3.28, 8.00 (doublet), 8.90, 9.16, 9.32, 9.63, 10.67, 12.07, 12.70, 13.2–13.4 (broad), 14.4 and 14.7 μ. 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 μ. The *para* compound had major peaks at 3.25, 9.18, 12.09, 13.20 and 14.45 μ. All major peaks of both *o*-chlorobiphenyl and *p*-chlorobiphenyl are present in the spectrum of the liquid product, and 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-μ peak of the mixture. The general shape of the peaks and the fine structure of the spectra are also consistent with the hypothesis that the liquid product is predominantly a 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 mixture.

A subsequent fraction (b.p. 125–160° at 0.01 mm.) solidified on cooling, yielding 12.7 g. of impure triphenylchlorosilane crystals melting at 75–90°. Crystallization of this material from petroleum ether (b.p. 60–90°) gave 7.58 g. (22% yield) of crystals melting at 89–93.5°. The recrystallized product showed a melting point of 95–97°.

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 titrations as described in the following section, was 62.4%.

Assay of Triphenylsilane.—Triphenylsilane was determined in the reaction mixture by measuring the volume of hydrogen evolved in the reaction with base.[10]

$$R_3SiH + R'OH \longrightarrow R_3SiOR' + H_2$$

The determination was carried out in a Zerewitinoff apparatus. The gas buret and reaction cell were thermostated 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% of the triphenylsilane present. Triphenylchlorosilane was found not to interfere.

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

Sealed Tube Reactions of Triphenylsilane and Di-*t*-butyl Peroxide in Halobenzenes.—Tubes made from Pyrex 15-mm. o.d. tubing were filled to about one-third their volume with various reaction mixtures, degassed by alternated 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 by hydrolysis of triphenylchlorosilane was titrated with standard alkali, using brom phenol blue as an indicator. Each tube contained 7.00 ml. of solution.

A tube containing 2 ml. each of chlorobenzene and di-*t*-butyl peroxide was heated at 135.0° for 25.5 hours, and the products were titrated in the same manner. No detectable acid was released, but a discoloration of the solution was noted.

Chain Transfer Constants.—The chain transfer constants of triphenylsilane and triethylsilane were determined by the methods developed by Mayo and his co-workers.[6,7] Styrene–silane solutions were thermally polymerized at 70.00 and 80.05° to about 10% conversion. The polystyrene was precipitated by adding methanol, redissolved in benzene and reprecipitated. This process was repeated, and the polystyrene sample was dried *in vacuo*. The number average molecular weights were determined from the intrinsic viscosities of the polystyrene solutions at 30.00° from the formula[7]

$$\overline{M} = 178{,}000[\eta]^{1.37}$$

developed by Mayo, Gress and Matheson. The chain transfer constants were determined by plotting the reciprocal degree of polymerization against the solvent–monomer ratio[6]

$$\frac{1}{\bar{P}} = C\frac{[S]}{[M]} + \frac{1}{\bar{P}_0}$$

The slope, C, of the resulting straight line is defined by Mayo as the chain transfer constant of the solvent.

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 authors wish to express their appreciation to Dr. M. Margoshes and Dr. R. M. Hedges, who recorded the spectra and contributed helpful information to their interpretation.

Results and Discussion

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, 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 phase hydrocarbon oxidations at "low" temperatures (50–150°) may well apply here.[12]

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

$$(C_6H_5)_2SiOOH \xrightarrow{\text{heat}} (C_6H_5)_3SiO\cdot + \cdot OH$$

$$(C_6H_5)_3SiO\cdot + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiOH + (C_6H_5)_3Si\cdot$$

The triphenylsilanol produced can thus be accounted for. No products illuminating the fate of the hydroxyl radical were isolated. Another pos-

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

sible reaction, in which the triphenylsilyl radical attacks the hydroperoxide initially formed, is

$$(C_6H_5)_3Si\cdot + (C_6H_5)_3SiOOH \longrightarrow (C_6H_5)_3SiOH + (C_6H_5)_3SiO\cdot$$

It would appear, therefore, that the triphenylsiloxy radical undergoes neither the disproportionation reaction characteristic of alkoxy radicals,[13] nor the rearrangement associated with tritoxy radicals.[14]

At sufficiently high oxygen pressures, the rate of radical initiated oxidation of moderately labile hydrocarbons is generally first order with respect to the hydrocarbon[15] in agreement with the above mechanism.[12]

The oxidation of triphenylsilane does not obey the first-order law under the conditions studied (see Fig. 1), 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 that an inhibitor is formed as the reaction progresses. Such a hypothesis would lead to the conclusion that oxygenated products, such as triphenylsilanol or triphenylsilyl hydroperoxide, could act as traps for the triphenylsilyl radicals. This property seems to be a characteristic one of silicon radicals. The inhibition begins to make itself evident at rather low conversions of triphenylsilane, causing a strong deviation from a first-order plot at conversions of less than 5%.

The identification of triphenylchlorosilane as a product of the reaction between di-*t*-butyl peroxide and triphenylsilane in chlorobenzene shows another contrast between the behavior of triphenylsilyl radicals and hydrocarbon radicals. Chlorobenzene is generally inert toward most free radicals, serving as a solvent for radical reactions such as oxidation and the thermal decomposition of peroxides.[12] Phenyl radicals produced by the decomposition of benzoyl peroxide do, however, attack chlorobenzene to form a mixture of isomeric biphenyls.[16,17] The abstraction of a chlorine atom from a benzene ring is an unprecedented mode of reaction for free radicals.

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

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot + (C_6H_5)_3SiH \longrightarrow (CH_3)_3COH + (C_6H_5)_3Si\cdot$$

$$(C_6H_5)_3Si\cdot + C_6H_5Cl \longrightarrow (C_6H_5)_3SiCl + C_6H_5\cdot$$

$$C_6H_5\cdot + C_6H_5Cl - \ldots \longrightarrow \underset{\text{(isomers)}}{C_6H_5C_6H_4Cl} + \text{other products}$$

The observed formation of a mixture of monochlorobiphenyls (*ortho* and *para* isomers) lends support to such a scheme.[16]

The removal of the volatile products of the peroxide decomposition (acetone and *t*-butyl alcohol) as they are formed increased the yield of triphenylchlorosilane. This observation suggests a competition by the volatile products with chlorobenzene for the attentions of the triphenylsilyl radical. Such a competition again indicates high reactivity of the silyl radicals toward oxygen compounds, and further explains the deviation from first order kinetics previously indicated.

If the scheme presented above properly represents the reaction and no chain reaction is induced in the course of the aromatic substitution reaction represented by equation 16, the rate of formation of triphenylchlorosilane would be expected to follow the rate of decomposition of the peroxide. The first-order rate constant for the decomposition of di-*t*-butyl peroxide at 135° has been determined in several solvents at values ranging from 3.6–5.2 $\times 10^{-5}$ sec.$^{-1}$.[18] 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 II 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 experiment from the formula

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

Table III shows the results of the above calculations.

The trend away from first-order kinetics again suggests a competition of the oxygen-containing products for the triphenylsilyl radical. The introduction of benzophenone into a seventh sealed tube reduced the formation of triphenylchlorosilane to zero. This observation supports the same contention.

TABLE II

RATES OF FORMATION OF TRIPHENYLCHLOROSILANE

Tube	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

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, although less so than chlorobenzene, forming 25% of the theoretical quantity of acid-releasing material, as compared with 40% for the reaction carried out under the same conditions in chlorobenzene. Fluorobenzene forms acid to the extent of 4% of the theoretical, a small but definite effect.

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(13) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

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

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

(16) D. H. Hey, *J. Chem. Soc.*, 1947 (1952).

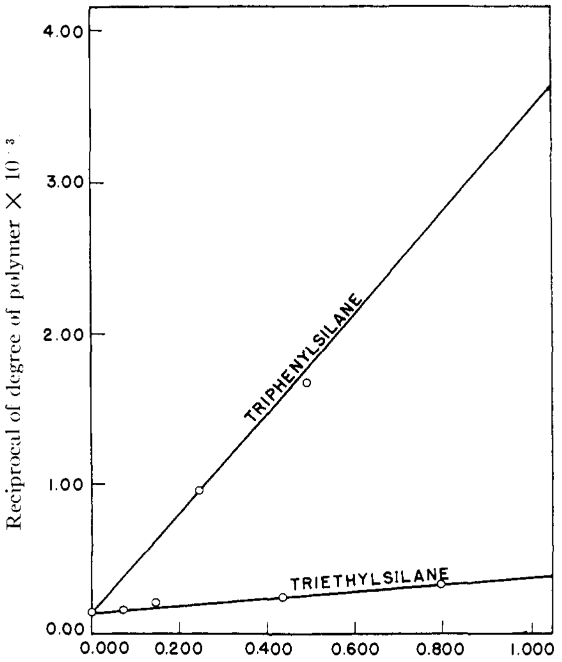
(17) R. R. Dannley, E. G. Gregg, R. E. Phelps and C. B. Coleman, THIS JOURNAL, **76**, 445 (1954).

(18) J. A. Raley, F. F. Rust and W. E. Vaughan, *ibid.* **70**, 1336 (1948).

Further sealed tube tests show 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.

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 low heat of formation and little reorganization energy. The high values of the silicon–halogen bond energies (135, 90 and 73 kcal./mole for the bonds involving fluorine, chlorine and bromine, respectively) given by Huggins[19] suggest that in the transition states for the halogen abstraction reactions considerable progress has been made in 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 toward oxygen-containing compounds.

The absence of hexaphenyldisilane, the product which would arise from the dimerization of triphenylsilyl radicals, from all product mixtures involving reactions of these radicals points to a high degree of reactivity for the latter 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.



Solvent/monomer ratio.

Fig. 2.—Evaluation of chain transfer constants.

Table III includes the chain transfer constants evaluated by the methods of Mayo and his associates.[6,7]

TABLE III

CHAIN TRANSFER CONSTANTS OF SILANES IN THE THERMAL POLYMERIZATION OF STYRENE

Silane	Temp., °C.	Chain transfer constant × 10^4
$(C_2H_5)_3SiH$	70.00	2.44 ± 0.12
$(C_2H_5)_3SiH$	80.05	1.3 ± 2.7
$(C_6H_5)_3SiH$	70.00	33.4 ± 1.2
$(C_6H_5)_3SiH$	80.05	36.8 ± 1.8

Figure 2 shows the plots at 70.00° obtained for triethylsilane and triphenylsilane. Table IV affords a comparison of the values here obtained for the two silanes with those determined for several hydrocarbons by Mayo and his co-workers.[6]

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 III. Mayo and co-workers[6,7] 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 the data of Gregg and Mayo,[6] Table IV, it can be seen that such a correlation is limited to processes involving the breaking of a carbon–hydrogen bond in the solvent. Benzene and aliphatic hydrogens possess low reactivity toward the growing polymer chain; benzylic hydrogens are markedly more active, increasingly so with increasing substitution. *t*-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.[6] However these effects are small when they are compared with the relative resonance energies of the S· species formed. Thus the energy of the transition state R· · ·H· · ·S 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 of the over-all reaction.

TABLE IV

CHAIN TRANSFER CONSTANTS OF VARIOUS SOLVENTS IN STYRENE POLYMERIZATION

Solvent	Transfer constant × 10^5, 60°	Solvent	Transfer constant × 10^5, 60°
Benzene	0.15	Pentaphenylethane	200,000
t-Butylbenzene	0.6	Cyclohexane	0.24
Toluene	1.25	*n*-Heptane	4.4
Ethylbenzene	6.7	Decalin	4
i-Propylbenzene	8.2	Carbon tetrachloride	900
Diphenylmethane	23	Triethylsilane[a]	22
Triphenylmethane	35	Triphenylsilane[a]	300
Fluorene	750		

[a] Extrapolated from values obtained at 70.00 and 80.05° in this work.

Mayo and Gregg[6] have pointed out that for most of the solvents presented in Table IV, increasing chain transfer constants correlate with decreasing activation energies and increasing fre-

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[19] M. L. Huggins, THIS JOURNAL, **75**, 4123 (1953).

quency factors with the former effect dominating. 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 could be attributed to greater resonance stabilization of the triphenylsilyl radical with respect to the triethylsilyl radical, or to the inductive influence of the phenyl groups on the Si–H bond strength. Uncertainty[6] as to the relative importance of the frequency factors and activation energies of the process preclude any possibility of estimating a reliable value of the resonance stabilization, if any, 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 IV. 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 at 79 kcal./mole, while carbon–hydrogen bonds have an energy of 88 kcal./mole on the same scale.[19] 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.

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Esterification of Carboxylic Acids by Dialkyl Phosphonates

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Aliphatic and aromatic carboxylic acids have been converted to alkyl esters in excellent yields by heating with dialkyl phosphonates.

The dealkylation of alkyl esters of phosphorous acid by hydrogen halides has been studied extensively in the past by Gerrard and co-workers.[2] The rates of this reaction for a given phosphite ester with respect to the hydrogen halide were found to decrease in the order: HI > HBr >> HCl, and with respect to a given hydrogen halide in the order: $(RO)_3P >> (RO)_2P(O)H > ROP(OH)_2$.[2b] The dealkylation of phosphites with hydrogen halides which proceeds according to the reaction sequence: $(RO)_3P + HX \rightarrow (RO)_2P(OH) + RX$; $(RO)_2P(O)H + HX \rightarrow ROP(OH)_2 + RX$; $ROP(OH)_2 + HX \rightarrow H_3PO_3 + RX$, can be used conveniently for the preparation of alkyl halides as well as mono- or dialkyl phosphites.[2a,c]

The acidolysis of the alkyl phosphites is not restricted to the hydrogen halides but was found in our study to occur also with the weakly acidic aliphatic and aromatic carboxylic acids. However, while the reaction with hydrogen halides proceeds at room temperature or below,[2a,c,3] the dealkylation by carboxylic acids requires higher reaction temperatures and is, in general, for preparative purposes best carried out by heating the mixture of alkyl phosphite and acid to temperatures above 100°. As in the reaction of an alkyl phosphite with a hydrogen halide, an alkyl group of the phosphite is replaced by hydrogen and transferred to the acid anion with the formation of the corresponding carboxylic acid ester. Although the rate of the acidolysis of a trialkyl phosphite is considerably faster than that of a dialkyl phosphonate (phosphite), the latter esters are of greater practical value as reactants for a rapid esterification of a carboxylic acid because of their ready availability from alcohols and phosphorus trichloride.[4] Since the acidolysis of an alkyl phosphite with excess acid results in the formation of phosphorous acid, each one of the alkyl groups of a dialkyl phosphonate can be utilized for esterification under the proper reaction conditions. By heating a carboxylic acid with 0.5 to 1 mole equivalent of a dialkyl phosphonate, esterification of an acid can be achieved readily in excellent yields without the use of a solvent or of excess alcohol as reaction medium as in most conventional esterifications. The resulting carboxylic acid esters can be separated easily from the acidolysis products of the phosphite by several simple manipulations, such as direct distillation, extraction or steam distillation. A similar method for the esterification of organic acids has been described recently by Sumrell and Ham,[5] who utilized the acidolysis of several alkyl orthosilicates by carboxylic acids for the preparation of the corresponding alkyl esters of the organic acids.

As the cleavage of alkyl phosphites by carboxylic

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[1] To whom requests for reprints should be addressed.

[2] (a) M. C. Berlak and W. Gerrard, *J. Chem. Soc.*, 2309 (1949); (b) W. Gerrard and E. G. G. Whitbread, *ibid.*, 914 (1952); (c) V. F. Cooke and W. Gerrard, *ibid.*, 1978 (1955).

[3] C. H. Campbell and D. H. Chadwick, THIS JOURNAL, **77**, 3379 (1955).

[4] H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

[5] G. Sumrell and G. E. Ham, THIS JOURNAL, **78**, 5573 (1956).