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Hydrogen–Halogen Exchange between Silanes and Triphenylmethyl Halides

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Triphenylmethyl halides will halogenate silanes at 25° in polar solvents. The reaction is rapid in partially chlorinated hydrocarbons, nitromethane, and nitrobenzene, slow in acetonitrile and benzene, and does not take place in ethers, hydrocarbons, or fully chlorinated hydrocarbons at room temperature. Benzhydryl and *t*-butyl halides are inactive but react to give hydrogen–halogen exchange in the presence of boron tribromide. A preliminary study of the kinetics of the reaction between triphenylchloromethane and triphenylsilane in benzene indicates probable first-order dependence of the rate on each reactant. A mechanism is suggested involving four-center attack of a carbonium ion–halide ion pair on the Si–H bond. Preparative applications of the reaction are also discussed.

Recently it has been shown that hydride abstraction by an existing carbonium ion may be used to generate new carbonium ions.[1] For example, a mixture of *t*-butyl bromide and boron tribromide, which generates the *t*-butyl carbonium ion, can be used to convert cycloheptatriene to tropenium ion.[2] In an attempt to generate siliconium ions by this method, triphenylsilane was added to a solution of triphenylcarbonium bromoborate in dichloromethane. An immediate reaction took place; the yellow color of the triphenylmethyl carbonium ions was discharged, and the silane was consumed as shown by the disappearance of the characteristic Si–H infrared band. However, the reaction did not lead to a siliconium ion product, but yielded instead a solution containing triphenylmethane, boron tribromide, and triphenylbromosilane

$$Ph_3C^+BBr_4^- + Ph_3SiH \longrightarrow Ph_3CH + BBr_3 + Ph_3SiBr$$

The latter two compounds were shown not to interact to form the siliconium bromoborate ion pair, either in dichloromethane or in other solvents.

Further experiments showed that the use of boron tribromide was necessary only when relatively unreactive organic halides were used. In appropriate solvents triphenylmethyl halides halogenate silanes smoothly at room temperature in the absence of added Lewis acid. The reaction can therefore be regarded as exchange of halogen for hydrogen between the organic compound and the silane

$$Ph_3CX + R_3SiH \longrightarrow Ph_3CH + R_3SiX$$

An investigation of the limits and generality of this facile reaction and a preliminary study of its mechanism are reported in this paper.

Experimental

Materials.—Triphenylchloromethane was prepared from triphenylcarbinol and acetyl chloride according to a standard method.[3] Triphenylbromomethane was obtained from hydrogen bromide and triphenylcarbinol in glacial acetic acid,[4] and triphenyliodomethane was prepared by addition of hydriodic acid to a solution of triphenylcarbinol in acetic anhydride.[5] These compounds were dried under vacuum for use in reactions with silanes. Other halides were commercial reagent quality compounds and were used as received, except that the allyl bromide and *t*-butyl bromide were redistilled before use.

Triphenylsilane and diphenylsilane were prepared by reduction of the corresponding chlorides with lithium aluminum hydride[6,7] and purified by vacuum distillation. Commercial trichlorosilane was purified by distillation. Triethylsilane was used as supplied by Peninsular ChemResearch, Inc.

All of the solvents used were of reagent quality. Benzene and acetonitrile were further purified by distillation, and tetrahydrofuran and dioxane were redistilled from lithium aluminum hydride before use. Other solvents were used without further purification.

Instrumentation.—Infrared spectra were determined using a Perkin-Elmer Model 237 grating spectrophotometer for the 650–4000 cm.$^{-1}$ region and a Perkin-Elmer Model 112 spectrophotometer with a cesium bromide prism for the 400–675 cm.$^{-1}$ region. Ultraviolet spectra were studied with a Cary Model 14 automatic recording spectrophotometer. Conductivities were determined using an Industrial Instruments, Inc., conductivity bridge Model RC-1b, and a conductivity cell with platinized platinum electrodes 1 cm. square, separated by a distance of 1 cm.

Attempted Reaction of Triphenylbromosilane with Boron Tribromide.—Addition of 3 to 4 drops of boron tribromide to a solution of 0.50 g. (0.0015 mole) of triphenylbromosilane in 10 ml. of dichloromethane did not produce coloration or heat evolution. The solution showed no detectable conductivity, indicating that it had a specific conductance of less than 4×10^{-7} ohm^{-1} cm.$^{-1}$. A comparison of the ultraviolet spectra of triphenylbromosilane in dichloromethane with that of solutions of triphenylbromosilane containing boron tribromide showed that no new bands occurred in the 4000–2000 Å. region. Attempts to precipitate a salt by addition of nonpolar solvents such as cyclohexane and pentane were unsuccessful. Evaporation of the solvent from solutions of triphenylbromosilane and boron tribromide resulted in the recovery of triphenylbromosilane. Similar experiments in benzene, acetonitrile, and tetrahydrofuran also failed to yield any evidence for the formation of ions.

Reaction of Triphenylsilane with Triphenylcarbonium Bromoborate in Dichloromethane.—A solution of triphenylcarbonium bromoborate was prepared from 0.5 ml. of boron tribromide and 0.32 g. (0.001 mole) of triphenylbromomethane in 10 ml. of dichloromethane.[2] To this solution was added 0.26 g. (0.001 mole) of triphenylsilane. The characteristic yellow color of the carbonium ions was immediately discharged and the specific conductance of the solution fell from 6.7×10^{-4} ohm^{-1} cm.$^{-1}$ to less than 4×10^{-7} ohm^{-1} cm.$^{-1}$. The triphenylsilane was consumed as evidenced by the disappearance of the Si–H band at 2150 cm.$^{-1}$ in the infrared region. When the mixture was evaporated to dryness under vacuum, the residue was found to consist of triphenylmethane and triphenylbromosilane, identified by comparison of their infrared spectra with authentic samples.

Reaction of Triphenylsilane with Triphenylbromomethane in Dichloromethane.—To 1.00 g. (0.0038 mole) of triphenylsilane in 7 ml. of dichloromethane was added 1.23 g. (0.0038 mole) of triphenylbromomethane. The triphenylsilane was consumed as shown by the disappearance of the Si–H band at 2150 cm.$^{-1}$. The infrared spectrum of this solution in the 400–675 cm.$^{-1}$ region was identical with that of a solution of triphenylmethane and triphenylbromosilane in dichloromethane, and showed the presence of the Si–Br band at 493 cm.$^{-1}$.

Preparation of Triphenylchlorosilane from Triphenylchloromethane and Triphenylsilane in Benzene.—In 40 ml. of dry benzene were dissolved 4.94 g. (0.019 mole) of triphenylsilane and 5.31 g. (0.019 mole) of triphenylchloromethane. Within 2 hr. a precipitate began to form. After standing overnight, the reaction was complete as indicated by the fact that the Si–H stretching band had disappeared from the infrared spectrum of the solution. The solid material was filtered from the solution and the mother liquor was concentrated and cooled to yield a second crop of the solid which was identified as triphenylmethane. A total of 3.75 g. (80%) was isolated. The remaining benzene was then evaporated under a stream of nitrogen and the residue was recrystallized from hexane, yielding 4.00 g. (71%) of pure triphenylchlorosilane. Evaporation of the remaining hexane yielded 2.5 g. of a mixture of triphenylmethane and triphenylchlorosilane.

An analogous reaction between triphenylbromomethane and triphenylsilane was shown to give triphenylmethane in 91% yield.

Preparation of Diphenylchlorosilane from Triphenylchloromethane and Diphenylsilane.—A solution of 5.0 g. (0.027 mole)

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(1) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(2) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

(3) "Organic Syntheses," Coll. Vol. III, edited by E. C. Horning, John Wiley and Sons, Inc., New York, N. Y., p. 841.

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(7) K. H. Benkesser, H. Landesmar, and D. J. Foster, *ibid.*, **74**, 648 (1952).

of diphenylsilane and 7.55 g. (0.027 mole) of triphenylchloromethane in 30 ml. of benzene was refluxed overnight under a nitrogen atmosphere. The solution was concentrated and cooled to recover triphenylmethane. The mother liquor was distilled, giving 5.80 g. (97%) of diphenylchlorosilane with a boiling point range of 99–101° (1 mm.). The halogen content of the center fraction was determined by hydrolyzing an ethereal solution of a sample with distilled water and titrating with standardized base to a brom cresol green end point.

Anal. Calcd. for $C_{12}H_{11}SiCl$: Cl, 16.3. Found: Cl, 16.3.

Diphenyldichlorosilane was prepared by the addition of two moles of triphenylchloromethane to one mole of diphenylsilane. A mixture of 5.0 g. (0.027 mole) of diphenylsilane and 15.1 g. (0.054 mole) of triphenylchloromethane in 35 ml. of dry benzene was refluxed overnight under an atmosphere of nitrogen. The solution was concentrated and cooled to give 11.8 g. (89%) of triphenylmethane. Vacuum distillation of the mother liquor gave 6.3 g. of material boiling at 115–125° at 1.75 mm. (93% based on complete conversion of the diphenylsilane to diphenyldichlorosilane). The halogen content was determined by titration of a hydrolyzed sample with standard base. The low chlorine analysis probably is due to the presence of some incompletely reacted diphenylchlorosilane in the product. The pot residue was found to contain 2.0 g. of triphenylchloromethane.

Anal. Calcd. for $C_{12}H_{10}SiCl_2$: Cl, 28.0. Found: Cl, 25.7.

The Systematic Study of the Exchange Reaction.—The infrared spectra of 0.18 M solutions of triphenylsilane in the various solvents studied were recorded to obtain standards for the Si–H band at 2150 cm.$^{-1}$. Equimolar amounts (approximately 0.0018 M) of the silane and of the halogen compound were then dissolved in 10 ml. of solvent. The reaction was followed by measuring the Si–H infrared absorbance. The 2150 cm.$^{-1}$ region was scanned within 10 min. after mixing and, if the reaction was not immediate and complete, at intervals thereafter. Disappearance of the Si–H band was taken to indicate completion of the reaction.

The hydrogen–halogen exchange reaction between some representative silanes and a number of different halides was studied in the solvent dichloromethane. Triphenylsilane was found to exchange rapidly at room temperature upon mixing with $(C_6H_5)_3CX$ (X = Cl, Br, and I). No reaction took place between triphenylsilane and $(C_6H_5)_2CHX$ (where X = Cl, Br) or with *t*-butyl bromide in dichloromethane. However, all of these halides gave rapid hydrogen–halogen exchange with triphenylsilane when boron tribromide was added to the solution. No exchange was observed with *t*-butyl iodide, allyl bromide, or triphenylmethyl isocyanate. Triethylsilane was found to exchange completely with $(C_6H_5)_3CX$ (X = Br, Cl) but not with *t*-butyl iodide or allyl bromide. Diphenylsilane exchanged either one or two hydrogens with triphenylbromomethane and triphenylchloromethane, depending on the amount of halide present. Complete exchange also occurred between trichlorosilane and triphenylchloromethane.

Several of the silane–halide systems were also studied in benzene, acetonitrile, carbon tetrachloride, and tetrahydrofuran (Table I). Finally, the triphenylbromomethane–triphenylsilane reaction was studied in a number of other solvents; results are shown in Table II.

Ultraviolet Spectra of Solutions of Triphenylbromomethane.—A 2.6 × 10^{-2} M solution of triphenylbromomethane in nitromethane gave two intense absorption peaks at 4050 and 4350 Å. This absorption has been shown to be due to the presence of the ion pair $(C_6H_5)_3C^+Br^-$, formed from the ionization of the triphenylbromomethane. The amount of ionization in this solvent has been calculated to be approximately 0.05% by Evans and co-workers.[8] These bands also appear, but with less intensity, in the absorption spectra of 0.10 M solutions of triphenylbromomethane in dichloromethane and in 1,2-dichloroethane. The percentage of dissociation of triphenylchloromethane in 1,2-dichloroethane was calculated by Evans to be approximately 0.005%,[9] and we estimate that the degree of dissociation in dichloromethane is very nearly the same. Solutions of triphenylbromomethane (approximately 0.10 M) in benzene, carbon tetrachloride, tetrahydrofuran, dioxane, and tetrachloroethylene did not show any characteristic carbonium ion absorption spectra in this region.

TABLE I

PERCENTAGE REACTION OF TRIPHENYLSILANE AND TRIETHYLSILANE WITH TRIPHENYLCHLOROMETHANE AND TRIPHENYLBROMOMETHANE IN VARIOUS SOLVENTS

Reactants	CH_2Cl_2, 10 min., 25°	C_6H_6, 24 hr., 25°	CH_3CN, 18 hr., 25°	CCl_4, 18 hr., 76°	THF, 18 hr., 65°
Ph_3CBr, Ph_3SiH	100	100	100	100	0
Ph_3CBr, Et_3SiH	100	80	100	100	0
Ph_3CCl, Ph_3SiH	100	97[a]	75	100	0
Ph_3CCl, Et_3SiH	100	70[a]	45	100	0

[a] HCl was present as a catalyst.

TABLE II

REACTION BETWEEN TRIPHENYLSILANE AND TRIPHENYLBROMOMETHANE IN VARIOUS SOLVENTS

Solvent	Dielect. const. (*t*, °C.)	Ref.	Temp., °C.	Time, hr.	Reacn., %
Cyclohexane	2.015 (25)	10	25	24	0
Dioxane	2.209 (25)	10	25	72	0
			101	9	100
Carbon tetrachloride	2.228 (25)	10	25	24	0
			76	18	100
Benzene	2.274 (25)	10	25	12	23
			25	48	60
Tetrachloroethylene	2.30 (25)	11	25	24	0
Carbon disulfide	2.64 (20)	10	25	24	0
Diethyl ether	3.97 (25)	10	36	18	0
Ethyl iodide	7.82 (20)	11	25	0.25	100
Tetrahydrofuran	8.20 (20)	12	67	18	0
Dichloromethane	9.08 (20)	10	25	0.25	100
Dichloroethane	10.36 (25)	10	25	.25	100
Nitrobenzene	34.82 (25)	10	25	.25	100
Nitromethane	35.87 (30)	11	25	.25	100

Kinetic Measurements on the Reaction between Triphenylsilane and Triphenylchloromethane in Benzene.—All measurements were carried out at 25°. The disappearance of silane or chloride was followed by infrared spectrophotometry. The effect of varying the triphenylchloromethane concentration while keeping the triphenylsilane concentration constant was studied by following the rate of disappearance of the silane Si–H absorbance at 2150 cm.$^{-1}$. Results are shown in Fig. 1. The effect of varying the triphenylsilane concentration while keeping the triphenylchloromethane concentration constant was studied by following the absorbance of the C–Cl band at 900 cm.$^{-1}$; results are given in Fig. 2. As a test of second-order dependence, the reciprocal of the optical density of the Si–H band was plotted *vs.* time, for equimolar mixtures of the silane and chloride in benzene. The results are shown in Fig. 3.

Early trials showed that the rate varied depending on the purity of the triphenylchloromethane. This variation was found to be due to catalysis of the exchange reaction by hydrogen chloride. Figure 3 also shows data for a 1:1 mixture of triphenylsilane and triphenylchloromethane containing added hydrogen chloride.

Results and Discussion

Trityl halides and silanes undergo exchange rapidly at room temperature in dichloromethane; qualitative observations indicate that the reaction rate increases in the order $Ph_3CCl > Ph_3CBr > Ph_3CI$. The four silanes which were studied, triphenylsilane, diphenylsilane, triethylsilane, and trichlorosilane, all undergo the reaction, but the arylsilanes react more rapidly than does triethylsilane. Diphenylsilane can exchange either one or two hydrogens, depending on the amount of trityl halide used.

Other halogen compounds tried included benzhydryl, allyl, and *t*-butyl halides. None of these reacted with triphenylsilane in dichloromethane in the absence of an added Lewis acid. However, upon addition of boron tribromide, which should convert these halides to carbonium ions,[2] all underwent the exchange reaction.

The solvent dependence of the reaction is summarized in Tables I and II. Reaction is complete within a few minutes at room temperature in most strongly ionizing solvents (nitromethane, nitrobenzene) and also in unsymmetrically halogenated hydrocarbons. It is slow at room temperature in acetonitrile and benzene, and

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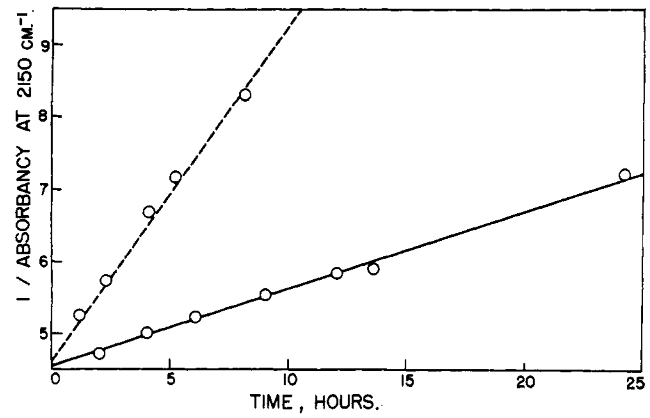

Fig. 1.—Plot of absorbancy of the Si–H stretching band (2150 cm.$^{-1}$) *vs.* time, showing the effect of varying the concentration of Ph_3CCl in the hydrogen–halogen exchange reaction: solid line, initial concentrations 0.173 *M* for each reactant; dashed line, initial concentrations 0.173 *M* in Ph_3SiH and 0.346 *M* in Ph_3SiCl, in benzene.

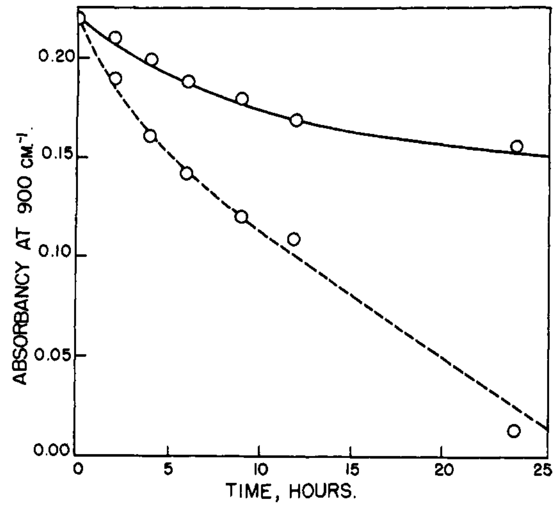

Fig. 2.—Plot of absorbancy *vs.* time for the C–Cl absorption band at 900 cm.$^{-1}$, showing the effect of varying the concentration of silane in the hydrogen–halogen exchange reaction: solid line, initial concentrations 0.173 *M* for each reactant; dashed line, initial concentrations 0.173 *M* in Ph_3CCl and 0.346 *M* in Ph_3SiH, in benzene.

there is no evidence of reaction at room temperature in ethers, carbon tetrachloride, or cyclohexane. The correlation of reaction rate with dielectric constant of the solvent is not complete (Table II). However, rapid reaction occurs in *just those solvents which have been shown to dissociate trityl halides into ion pairs.* Spectrophotometric studies have shown that triphenylchloromethane is partially ionized in nitroalkanes,[8] nitrobenzene,[13] dichloroethane,[9] and other partially chlorinated hydrocarbons. Dissociation of trityl halides by solvents of the latter type, despite their relatively low dielectric constants, is thought to involve a specific solvation effect. No ionization of trityl halides takes place in tetrachlorethylene,[9] ether, or carbon disulfide, nor does hydrogen–halogen exchange take place in these solvents. Very slight ionization occurs in benzene,[13] and in this solvent room-temperature exchange is slow. Tritvl bromide is known to be dissociated to a greater extent than trityl chloride,[14] and still greater ionization would be expected for the iodide. Thus all of the evidence is consistent with the hypothesis that carbonium ions are intermediates in the reaction.

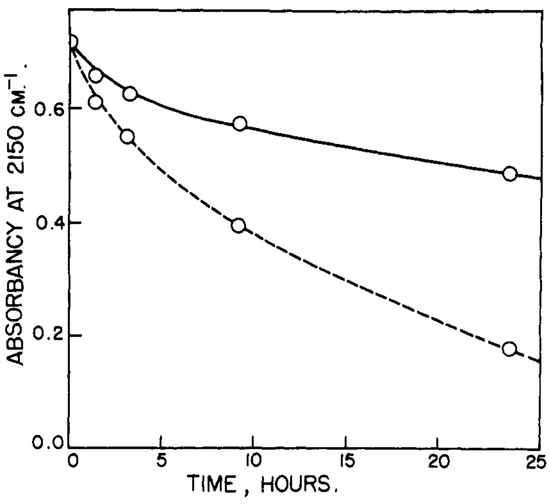

Fig. 3.—Plot of reciprocal of absorbancy of Si–H stretching absorption band (2150 cm.$^{-1}$) *vs.* time: solid line, initial concentrations 0.173 *M* each for Ph_3SiH and Ph_3CCl in benzene; dashed line, same initial concentrations of reactants with HCl present at 0.96 *M*.

Exchange was also shown to occur in two of the poor ionizing solvents (carbon tetrachloride and dioxane) at elevated temperatures. Related high-temperature halogenations of silanes by organic halides have been reported previously. Hydrogen–halogen exchange takes place when triethylsilane is refluxed in allyl bromide for 15 hr.,[15] and triethylbromosilane is obtained in 10% yield when triethyslilane is refluxed in *n*-propyl bromide for 12 hr. The same silane reacts vigorously with *n*-hexyl chloride in the presence of aluminum chloride.[16] Acyl halides have been reported to halogenate silanes in ether,[17] but the actual exchange apparently does not take place until after the solvent is removed.[18] Many of these halogenation reactions may also take place *via* carbonium or acylonium ion intermediates, but it is also possible that a different mechanism becomes operative at higher temperatures.

Results of some preliminary studies of the kinetics of the reaction between triphenylsilane and triphenylchloromethane are shown in Fig. 1–3. The reaction shows approximately first-order kinetic dependence on both of these reactants, so the SN1 mechanism seems highly unlikely. The fact that a straight line is obtained in the plot of 1/absorbancy *vs.* time for a solution containing equimolar amounts of the reactants (Fig. 3) is consistent with second-order kinetics for the reaction. The second-order rate constant obtained from this graph is 0.14 M^{-1} hr.$^{-1}$.

A mechanism involving simultaneous nucleophilic attack of halide on silicon and electrophilic attack on hydrogen by the carbonium ion is reasonable. Such a mechanism would probably take place *via* a four-center transition state

$$Ph_3SiH + Ph_3C^+Cl^- \xrightarrow{\text{benzene}} \left[\begin{array}{ccc} Ph_3Si & -\,-\,- & H \\ \vdots & & \vdots \\ Cl^- & & C^+Ph_3 \end{array}\right] \longrightarrow Ph_3SiCl + Ph_3CH$$

The more rapid reaction for phenyl- than for alkylsilanes indicates that the silicon may become somewhat

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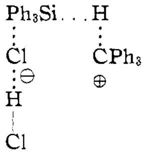
more positive in going to the transition state.[19] The reaction is markedly catalyzed by added hydrogen chloride, but the catalyzed reaction still seems to show first-order dependence on silane and halide (Fig. 3). Hydrogen chloride may possibly serve to promote the dissociation of the triphenylmethyl halide into the carbonium ion salt $Ph_3C^+ HCl_2^-$,[20] which would also function as an ion pair in the transition state



A similar four-center mechanism has been suggested by Russell for the reaction of silanes with alkyl halides in the presence of aluminum chloride.[21] The reaction of trityl halides with silanes may have some preparative value. Other methods are available for the conversion of silanes to silyl halides, but the conditions required are generally more drastic than those for the trityl halide reaction which may therefore be useful in halogenating sensitive silicon–hydrogen compounds. Also, it is often difficult to synthesize compounds containing both hydrogen and halogen bonded to silicon. Methods which have been used include the addition of a deficiency of a Grignard reagent to a halide such as $SiHCl_3$[22,23] or the reaction of a mixture of a dichlorosilane with a dihydride in the presence of aluminum chloride.[16] A troublesome separation step is necessary to obtain the desired product in either of these methods. The reaction of equimolar amounts of triphenylchloromethane and diphenylsilane in benzene led to a good yield of diphenylchlorosilane, Ph_2SiHCl, and it is possible that the reaction will be generally useful for the preparation of such mixed hydride–halides. For preparative purposes, the use of benzene as a solvent is especially convenient because nearly all of the triphenylmethane by-product precipitates from this solvent when the reaction mixture is concentrated.

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Retarded Autoxidation and the Chain-Stopping Action of Inhibitors

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Oxidation of purified *cis*-1,4-polyisoprene, inhibited with secondary aromatic amines and a hindered phenol, was studied to determine if the kinetic isotope effects previously observed with deuterated oxidation inhibitors could be demonstrated at an earlier stage of the reaction. A linear plot for oxygen absorption *vs.* time demonstrated isotope effects in the initial stage of oxidation consistent with a rate-controlling hydrogen-abstraction process for the chain-stopping action. The decrease in apparent observed isotope effect with increasing inhibitor concentration and increasing oxidation temperature has been confirmed. This, and the observed change in inhibitor action from antioxidant to pro-oxidant with increasing inhibitor concentration, indicates that direct oxidation of inhibitor is a significant initiation process. The oxygen-absorption plots obtained in this study showed two discrete stages of retarded oxidation. The amount of oxygen absorbed at the well defined break between the initial stage and the faster second stage was independent of temperature and inhibitor concentration. It is suggested that this phenomenon is due to the onset of bimolecular hydroperoxide decomposition as a major initiation process. This hypothesis is supported by the observation that oxidation of samples preoxidized to the second stage, and then heated in a nitrogen atmosphere to decompose peroxides, again showed two constant-rate stages of retarded oxidation.

Introduction

The free-radical chain mechanism of autoxidation of organic materials is well established.[1,2] In the absence of oxidation inhibitors or added initiators, the only important initiation process involves peroxide decomposition, and the principal termination reaction involves the combination of two peroxy radicals. In the presence of materials which inhibit or retard the reaction of oxygen with organic substances, important changes occur in both the initiation and termination processes. Recent reviews on the subject of inhibition of oxidation are available.[3,4]

The rate of autoxidation of hydrocarbons in the absence of inhibitors is nearly independent of oxygen concentration,[2] but the rate of retarded oxidation in the presence of antioxidants increases in a regular fashion as the partial pressure of oxygen is increased.[5] This change reflects a shift in the initiation process from exclusively peroxide initiation to include reactions involving direct attack of oxygen upon the antioxidant, and possibly upon the hydrocarbon. The formation of free radicals as a result of direct oxidation of the inhibitor is also indicated by the observation that antioxidants often become pro-oxidants at concentrations greater than the optimum. Additional evidence for this reaction is provided in this paper and related studies.[6,7]

The important termination reaction in the mechanism of retarded autoxidation is the chain-stopping action of inhibitors. The widely used hindered phenol and secondary arylamine types probably function by donating hydrogen to a peroxy free radical. The resulting inhibitor free radical may combine with another $RO_2\cdot$ or it may participate in a chain-transfer process. Various kinetic studies[8,9] and product isolations[9-11] have given results that are in agreement with this mechanism.

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