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ORGANOSILICON COMPOUNDS
XLI*. A KINETIC STUDY OF THE GAS-PHASE REACTION BETWEEN SILICON HYDRIDES AND ARYL CHLORIDES

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INTRODUCTION

It has been known for several years from the work of A. D. Petrov and his colleagues that passage of chlorobenzene and trichlorosilane at atmospheric pressure through a hot tube at 520–700° gives four major products, *viz.* phenyltrichlorosilane, hydrogen chloride, tetrachlorosilane, and benzene[2,3,4]. The first two products are formed together in one kind of reaction, termed condensation, denoted by *C*, and the other two are formed together in a different reaction, termed reduction, denoted by *R*[3].

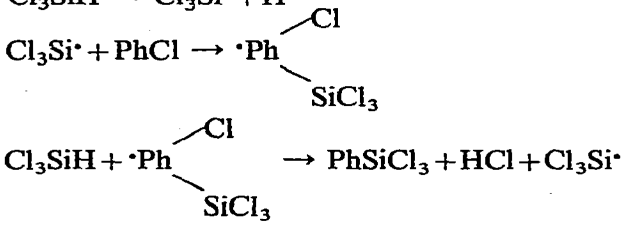
$$PhCl + Cl_3SiH \rightarrow \begin{cases} PhSiCl_3 + HCl & (C) \\ PhH + SiCl_4 & (R) \end{cases}$$

Numerous aryl halides and silicon hydrides have been shown to undergo similar reactions (see, for example, refs. 4–6).

The Russian workers concluded from their studies that the initial step is homolytic dissociation of the silicon hydride, and that this is followed by two simultaneous chain processes. The first, leading to condensation, involves attack of the $Cl_3Si^{\bullet}$ radical on the aromatic ring, and the second leading to reduction, involves abstraction of a chlorine atom from the ring**: *e.g.*

$$Cl_3SiH \rightarrow Cl_3Si^{\bullet} + H^{\bullet}$$

(*i*)



$$Cl_3Si^{\bullet} + PhCl \rightarrow {}^{\bullet}Ph{<}^{Cl}_{SiCl_3}$$

$$Cl_3SiH + {}^{\bullet}Ph{<}^{Cl}_{SiCl_3} \rightarrow PhSiCl_3 + HCl + Cl_3Si^{\bullet}$$

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* For Part XL see ref. 1.

** We prefer to regard the intermediate in process (*i*) as a σ-complex. The Russian authors write it as a π-complex, believing, as we think wrongly, that formation of a σ-complex is ruled out by the observation that isomeric mixtures are not formed in reactions of XC_6H_4Cl compounds (*e.g.* X = Me)[3]. Of course, a π-complex may possibly be formed on the way to a σ-complex.

(*ii*) $Cl_3Si^{\bullet} + PhCl \rightarrow Cl_4Si + Ph^{\bullet}$

$Ph^{\bullet} + Cl_3SiH \rightarrow PhH + Cl_3Si^{\bullet}$

A kinetic study by Bykovchenko and his colleagues under the flow conditions used by Petrov *et al.*, revealed that the trichlorosilane–chlorobenzene reaction is second order overall at 620°, with an overall activation energy of 51 kcal/mole, and that reaction is inhibited by nitric oxide, propene, or cyclohexene[7,8]. From the effect of cyclohexene it was calculated that the reaction is a radical-chain with a mean length of 5.8 at 520°.

We describe below the results of a kinetic study we have made of this reaction in a static system at rather lower temperatures.

RESULTS

We employed a static system at 380–575°, with initial partial pressures of each reactant of 15–100 mm. The reaction mixture could be sampled for gas-chromatographic analyses at any time during a run, and so the rates of disappearance of reactants and appearance of products could be measured.

Chlorobenzene was shown to be stable under the reaction conditions (*cf.* ref. 9), but trichlorosilane was found to decompose slowly above 500° to give mainly tetrachlorosilane and hydrogen; the first order rate constant was *ca.* 1.4×10^{-4} sec^{-1} at 555°. At 500° the rate of this reaction is about 5% of that of trichlorosilane with chlorobenzene. Because of this pyrolysis, the rate of disappearance of chlorobenzene was usually taken as the measure of the rate of the chlorobenzene–trichlorosilane reaction.

It was found that equimolar amounts of phenyltrichlorosilane and hydrogen chloride were formed, and also equimolar amounts of benzene and tetrachlorosilane (after allowance for some formation of the latter from trichlorosilane). These four compounds accounted for more than 97% of the reaction products.

The products were found not to react with one another. The rates of condensation and reduction and the final *C/R* ratio were derived from the analyses for phenyltrichlorosilane and chlorobenzene. A four-fold change in the initial ratio of trichlorosilane to benzene at 504° and at 535° caused the *C/R* ratio to change only by 8–10%, and this variation cannot be regarded as significant. The *C/R* ratio seems to decrease somewhat with increasing temperature, at least in the upper part of the temperature range; thus for initial pressures of 50 mm in each reactant, the ratios after 25% of reaction were: 3.1 at 413°; 2.8 at 446°; 2.8 at 464°; 2.7 at 504°; 2.3 at 534°.

The great majority of the runs were carried out in an unpacked quartz vessel, but the effect of the surface was investigated by using also (*a*) an unpacked Pyrex glass vessel, (*b*) a similar vessel packed with sufficient Pyrex tubing to give a 15-fold increase in the surface/volume ratio, and (*c*) a quartz vessel packed with quartz wool to give a very large increase in surface/volume ratio. In the upper part of the temperature range the rate was the same in all the vessels, while in the bottom 110° of the range the rate was about 10% larger in the packed than in the unpacked vessels.

Nitric oxide was found to be an effective inhibitor over the whole temperature range; *e.g.* at 500°, 12.5% of nitric oxide reduced the initial rates of disappearance of chlorobenzene and trichlorosilane to 8% of their normal value. There was no signif-

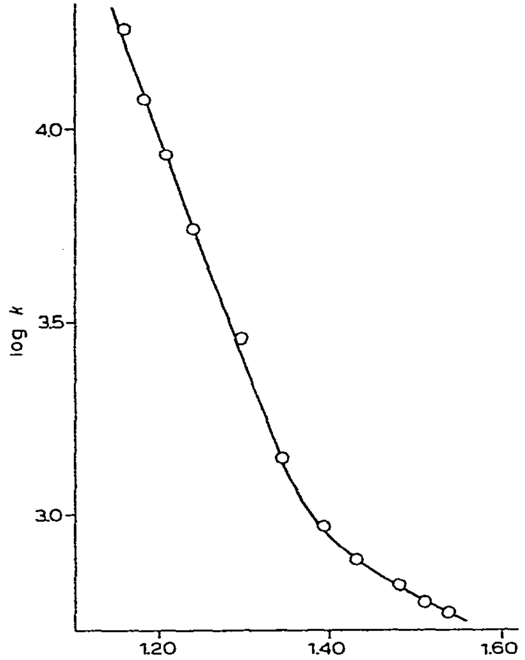

Fig. 1. Arrhenius plot for the Cl_3SiH–PhCl reaction.

icant change in the *C/R* ratio.

The activation energy was found to vary markedly with the temperature. The Arrhenius plot (Fig. 1) shows two distinct reasonably linear regions; these correspond to overall activation energies of 6.4 kcal/mole at 380–430° and 26.5 kcal/mole at 470–575°, with corresponding preexponential factors of $10^{4.83}$ and $10^{7.9}$ $l \cdot mole^{-1} \cdot sec^{-1}$, respectively. In the upper range the observed variation of the C/R ratio is consistent with an activation energy of about 26 kcal/mole for the condensation and 28 kcal/mole for the reduction.

The Arrhenius plot indicates that a change in mechanism occurs in the region of 440–460°, and in agreement with this, the order of reaction changes in this region.

TABLE 1

DEPENDENCE OF RATE OF PhCl–Cl_3SiH INTERACTION ON INITIAL PRESSURES AT 427.0°

$P_0(HSiCl_3)$ (*mm*)	$P_0(PhCl)$ (*mm*)	$10^5k(Cl_3SiH)$ (sec^{-1})	$10^5k(PhCl)$ (sec^{-1})
15	50		9.2
20	50		9.2
25	50	8.5	8.8
50	50	10.0	7.9
75	50	8.5	8.8
50	.15	2.9	
50	100	20.0	7.9

At 427° the reaction is overall of first order, zero order with respect to trichlorosilane and first order with respect to chlorobenzene. This is shown by the data in Table 1, which shows that the rates of disappearance of chlorobenzene, expressed as a first order rate constant $k(\text{PhCl})$, is unaffected by change in the trichlorosilane concentration, but the rate of disappearance of trichlorosilane, expressed as a first order rate constant $k(\text{HSiCl}_3)$, depends linearly on the concentration of chlorobenzene.

At 555° the usual second-order plots of time *versus* log ([PhCl]/[HSiCl_3]) (allowance being made for disappearance of trichlorosilane by pyrolysis) were linear to more than 7 half-lives. At this temperature the results of separate variation of the initial concentrations of trichlorosilane and chlorobenzene indicate that the order is approximately one with respect to each reactant.

Other reactant pairs

(*a*) *The high temperature region.* The reactants Cl_3SiH and p-$\text{MeC}_6\text{H}_4\text{Cl}$ gave the expected products; *viz.* p-$\text{MeC}_6\text{H}_4\text{SiCl}_3$, PhMe, SiCl_4, and HCl; the C/R ratio was 3.2 ± 0.5 at 520°. The Arrhenius parameters for the second-order reaction in the range 435–555° were given approximately by $k = 10^{5.6} \exp(-22{,}000/RT)\ \text{l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$. The second order rate constant at 555° was $6.24 \times 10^3\ \text{l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$, *i.e.* 0.73 times that for the Cl_3SiH–PhCl reaction. Consistently, when a mixture of equal concentrations of chlorobenzene and *p*-chlorotoluene was brought into reaction with a deficiency of trichlorosilane at 520° the chlorobenzene removed the hydride 1.2 times as fast as did the *p*-chlorotoluene.

With the reactants Cl_3SiH and p-$\text{CF}_3\text{C}_6\text{H}_4\text{Cl}$ the C/R ratio was 1.30 at 480°, and in the range 430–520° the second-order rate constant was given approximately by the expression $k = 10^{10.2} \exp(-31{,}200/RT)\ \text{l}\cdot\text{sec}^{-1}\cdot\text{mole}^{-1}$. The reaction was about eight times as fast as the trichlorosilane–chlorobenzene reaction at 480°.

With the reactants Me_3SiH and PhCl, the product PhSiMe_3 seemed to react further, and a meaningful C/R ratio could not be obtained. At 484° the amount of benzene present after the disappearance of 50% of the chlorobenzene was 2.7 times as large as in Cl_3SiH–PhCl reaction. Only the expected condensation and reduction products were found, and it seems likely that the secondary reaction involves cleavage of the phenyltrimethylsilane by hydrogen chloride to give benzene and chlorotrimethylsilane. The disappearance of chlorobenzene was first order with respect to both trimethylsilane and chlorobenzene at 555°; the Arrhenius parameters for this second-order disappearance of chlorobenzene in the range 454–555° are given approximately by the expression $k = 10^{8.1} \exp(-23{,}500/RT)\ \text{l}\cdot\text{sec}^{-1}\cdot\text{mole}^{-1}$.

The reaction between bromobenzene and trichlorosilane was examined briefly at 500°. The reaction was about 10 times as fast as that with chlorobenzene. The products included phenyltrichlorosilane and benzene in a ratio of approximately $\frac{1}{10}$, along with mixed chlorobromosilanes, presumably formed by disproportionation of the initially formed trichlorobromosilane. It was found that bromobenzene undergoes pyrolysis at a significant rate at 520°, and so the mechanism of reaction may be different from that involving chlorobenzene.

(*b*) *The low temperature region.* At 427°, the reaction of chlorobenzene with methyldichlorosilane or trimethylsilane was of first order in chlorobenzene and zero order in the silicon hydride, and the rate in both cases was within experimental error the same as in the trichlorosilane reaction. With triethylsilane the orders were the same, but the rate was 5.8×10^{-4} l·sec^{-1}·mole^{-1}, *i.e.* half that for the reactions involving the other hydrides*.

DISCUSSION

Over the whole temperature range for the Cl_3SiH–PhCl reaction the same products were formed, and in much the same ratio, the reaction was substantially inhibited by nitric oxide, and the rate was effectively independent of the surface/volume ratio. These features are all consistent with gas-phase propagation of the radical chains proposed by Petrov and his colleagues[3], and shown in reactions (2)–(5).

$$Cl_3SiH + Wall \rightarrow [Cl_3SiH^{\cdot}\,Wall] \rightarrow [Wall^{\cdot}\,H] + Cl_3Si^{\cdot} \quad (1)$$

$$PhCl + Cl_3Si^{\cdot} \rightarrow PhSiCl_3 + Cl^{\cdot} \quad (2)$$

$$Cl_3SiH + Cl^{\cdot} \rightarrow HCl + Cl_3Si^{\cdot} \quad (3)$$

$$PhCl + Cl_3Si^{\cdot} \rightarrow SiCl_4 + Ph^{\cdot} \quad (4)$$

$$Cl_3SiH + Ph^{\cdot} \rightarrow PhH + Cl_3Si^{\cdot} \quad (5)$$

$$Cl_3Si^{\cdot} + [H^{\cdot}\,Wall] \rightarrow Cl_3SiH + Wall \quad (6)$$

The product ratio C/R would be given by k_2/k_4, and would thus be independent of the initial proportions of reactants, as observed. It would also be unaffected by partial suppression of chains by added nitric oxide.

In considering the nature of the initiating process, we note that for initiation by homogeneous gas-phase dissociation of either reactant or by a homogeneous bimolecular reaction between the reactants produce radicals, the overall activation energy could not be less than half the bond dissociation energy of the Ph–Cl or X_3Si–H bond, whichever is the lower. For the Ph–Cl bond this energy is in the region of 94 kcal/mole. Values of $D(X_3Si\text{–}H)$ are available only for Me_3SiH, and they are conflicting, ranging from 88 to 74 kcal/mole[10], with 84 kcal/mole as the most recent value[11]. The value for Cl_3SiH is unlikely to be much less than 84 kcal/mole. Gas-phase dissociation of the hydrides cannot, therefore, be the primary step in the high temperature range. In the low temperature range the very low value of the activation energy leaves no doubt that initiation is at the surface, and we assume in subsequent discussion that this is also the case in the high temperature range. In both cases termination of the chains must also occur at the walls to explain in the absence of dependence of rate on the surface/volume ratio in a given type of vessel, and since the ratio is also unaffected by change from glass to quartz vessels, at least in the lower temperature range, it seems probable that the main termination step (6) is the reverse of the initiation step (1).

It is likely that in the lower temperature range initiation occurs by adsorption and dissociation of trichlorosilane on a very small number of highly active sites on the wall followed by desorption of radicals into the gas-phase. Such sites would be fully occupied by a very small number of trichlorosilane molecules, and the rate of initiation

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* The triethylsilane decompose too rapidly at higher temperatures to permit useful study of its reaction with chlorobenzene in the higher temperature range.

would be independent of the trichlorosilane concentration. The overall rate of disappearance would then be given by:

$$\frac{-\mathrm{d}[\mathrm{PhCl}]}{\mathrm{d}t} = \frac{k_1(k_2+k_4)}{k_6}[\mathrm{PhCl}]$$

Such a mechanism does not require that the rate also be independent of the nature of the silicon hydride, since the values of k_1, k_2, k_4, and k_6 could all be different for different hydrides. However, in processes of such low activation energy it would not be surprising to find no significant difference between similar hydrides. The somewhat lower rate observed for triethylsilane could be attributed to hindrance to adsorption of this hydride by the relatively bulky ethyl groups.

At higher temperatures it seems that dissociation of hydride can occur, with markedly greater activation energy, at a greater number of much less active sites. Only a fraction of such sites would be occupied, and the rate of initiation would thus be proportional to the concentration of the hydride. The rate of reaction under these conditions would be given by:

$$\frac{-\mathrm{d}[\mathrm{PhCl}]}{\mathrm{d}t} = \frac{k_1(k_2+k_4)}{k_6}[\mathrm{PhCl}][\mathrm{Cl_3SiH}]$$

Some variation of the C/R ratio with temperature would be expected, since reactions (2) and (4), the relative rates of which determine this ratio, are unlikely to have identical energies of activation.

The results for the compounds p-MeC_6H_4Cl and p-$CF_3C_6H_4Cl$ throw no further light on the mechanism. We merely note that with the mechanism proposed above the effects of the nuclear substituents on the overall rate, activation energy, and C/R ratio would be exerted wholly through reactions (2) and (4).

A third mechanism of initiation seems to be involved at higher temperatures still, because in a flow system at 560–680° Bykovchenko *et al.* observed an activation energy of 51,000 kcal/mole for the second-order Cl_3SiH–PhCl reaction and one of 44,000 kcal for the $MeCl_2SiH$–PhCl reaction[7,8]. Such values would be consistent with initiation by homogeneous gas-phase dissociation of the hydride.

EXPERIMENTAL

Standard high vacuum apparatus was used; this was of Pyrex glass except for the reaction vessel, which was usually a quartz cylinder of about 750 ml, housed in an electric furnace controlled by a platinum resistance thermometer and proportional controller; temperatures were measured by a chromel–alumel thermocouple. Samples could be transferred directly from the reaction vessel to a gas chromatograph through a stainless steel valve[12]; the valve and the connecting tubes were heated electrically to keep all reactants and products in the vapour phase. The gas chromatograph consisted of a copper column packed with 5% silicone oil on kieselguhr and a Gow-Mac thermal conductivity detector. The column was in a low heat capacity oven, and a simple manually controlled temperature-programming cycle was usually employed in analyses.

The reactants were stored in the apparatus under vacuum as liquids. A run was started by distilling some of each reactant into a bulb adjacent to the reaction vessel, heating it to about 200°, allowing sufficient time for mixing, then expanding the mixture into the reaction vessel. Pressures were measured by a glass spiral manometer.

All the compounds used in this work were prepared by standard methods or obtained commercially, and were purified by fractionation and high vacuum distillation where necessary, and checked for purity by gas chromatography.

Pyrolysis

The following rates of disappearance, expressed as first-order rate constants, were observed at 555° for silicon hydrides on their own: Cl_3SiH, 14×10^{-5}; Me_3SiH, 5.8×10^{-5}; Et_3SiH, 120×10^{-5} sec^{-1}. For bromobenzene at 520° a value of 8.3×10^{-4} sec^{-1} was observed.

Effect of surface

The following rates of removal of chlorobenzene, expressed as first-order rate constants, were observed for the Cl_3SiH–PhCl reaction. (*i*) In the standard quartz vessel: 5.7×10^{-5} at 401°; 50×10^{-5} at 526°; 146×10^{-5} sec^{-1} at 581°. (*ii*) In the same vessel packed with quartz wool: 5.7×10^{-5} at 401°; 54×10^{-5} at 526°; 144×10^{-5} sec^{-1} at 581°. (*iii*) In a Pyrex glass vessel: 5.7×10^{-5} at 401°; 6.9×10^{-5} at 419°; 8.8×10^{-5} at 450°; 22×10^{-5} sec^{-1} at 489°. (*iv*) In the same vessel packed with Pyrex glass tubing to give a 15-fold increase in the surface/volume ratio: 7.6×10^{-5} at 401°; 7.8×10^{-5} at 419°; 8.8×10^{-5} at 450°; 21×10^{-5} sec^{-1} at 489°.

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SUMMARY

A kinetic study has been made of the reaction between chlorobenzene and trichlorosilane in a static system at 380–575°. In the 380–430° region the reaction has an activation energy of only 6.4 kcal/mole, and is of first order in chlorobenzene and zero order in trichlorosilane, whereas at 470–575° it has an activation energy of 26.5 kcal/mole and is of first order in both reactants. Over the whole temperature range the reaction is substantially inhibited by nitric oxide, and the rate is effectively independent of the surface to volume ratio of the container. It is suggested that reaction is initiated by dissociation of the Si–H bond at the surface, but that different modes of adsorption operate in the two distinct ranges. Radical chains are then propagated in the gas phase and terminated at the surface.

The reactant pairs *p*-MeC_6H_4Cl–Cl_3SiH, *p*-$CF_3C_6H_4Cl$–Cl_3SiH, PhCl–Me_3SiH, PhCl–$MeCl_2SiH$, and PhCl–Et_3SiH have also been studied. In the low temperature range the hydrides Me_3SiH and $MeCl_2SiH$ react with chlorobenzene at the same rate as trichlorosilane.

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