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THE MECHANISM OF HYDRIDE TRANSFER FROM SILICON TO A CARBENIUM ION IN A WEAKLY NUCLEOPHILIC MEDIUM

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Summary

The reaction of hydrosilanes with triphenylmethylium hexafluoroantimonate in methylene chloride leads to the replacement by fluorine of hydrogen bound to silicon, and involves at least three steps. The first is hydride transfer leading to the formation of a positively-charged silicon intermediate. The second is the formation of an uncharged intermediate, which reacts in the third step to give the fluorosilane. Free carbenium ions and the corresponding ion pairs show similar reactivity towards hydrosilanes, indicating that the counter ion plays no role in hydride transfer. Effects of substituents at silicon on the reactivity are complex, and not those which might be expected if a simple trivalent silicenium ion were formed in the rate-determining step.

Introduction

Hydride transfer from carbon leads to formation of carbenium ion species and thus silicenium ion might be expected to result from analogous hydride transfer from silicon. Failure of early attempts of generating silicenium ions in this way * [1], taken together with results of kinetics and stereochemical studies [5,6] led instead to the concept of a synchronous mechanism involving a four-centre transition state in which the silicon atom simultaneously donates a hydride ion and forms a new bond with a nucleophile. The kinetic studies have been so far carried out in the presence of moderate or fairly strong nucleophiles such as chloride ion [5] or solvent acetic acid [6], and possibly other nucleophiles adventitously present, and such conditions might favour the synchronous mechanism. On the other hand the stereochemical course of the reaction was found to be dependent

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* Recent results which were taken to indicate the formation of silicenium ions [2,3] have now been shown to have a different interpretation [4].

on the solvent [7], which implies that the four-centre mechanism may not be the only route for hydride transfer from silicon, and the possibility of the formation of a silicocation intermediate has been also considered [8].

We have studied the kinetics of the reaction between organosilicon hydrides and trityl hexafluoroantimonate in methylene chloride solution. This system has at least two advantages over the previously studied systems

(1) It allows the study of hydride transfer from silicon in a medium of relatively low nucleophilicity. The trityl salt is stable * and fully ionised in weakly nucleophilic methylene chloride. The counter-ion SbF_6^- is a much poorer nucleophile than Cl^- and even poorer than the commonly used ClO_4^- [2—4,10]. Moreover the trityl ion is known to form colorless complexes reversibly with water, alcohols and ethers [11], and so these nucleophiles can be detected if present in the system [12].

(2) It allows analysis of the rate of hydride transfer in terms at the concentrations of free carbenium ions and ion pairs, since the dissociation constant of $Ph_3C^+ SbF_6^-$ in CH_2Cl_2 has been recently determined [13,14]. The concentrations of the possible carbenium ion species were unknown in earlier studies of hydride transfer from silicon.

Results and discussion

By analogy with the reaction with trityl tetrabromoborate, the reaction of silicon hydrides with trityl hexafluoroantimonate was assumed to proceed as follows:

$$Ph_3C^+ SbF_6^- + H\text{—}Si\equiv \rightarrow Ph_3CH + F\text{—}Si\equiv + SbF_5$$

The validity of this assumption was confirmed by identification of triphenylmethane and the appropiate fluorosilane in the products by combined gas chromatography/mass spectrometry. Quantitative GLC analysis proved that the fluorosilane was formed quantitatively from the hydride. However the rate of formation of the fluorosilane was distinctly lower than the rate of disappearance of the hydrosilane (see Fig. 1). This indicates that the reaction involves a multistep mechanism, and precludes synchronous replacement of hydrogen at silicon by fluorine, since the fluorosilane must be formed after the hydride transfer.

The kinetics of the hydride transfer step have been studied spectroscopically by monitoring the decrease of the absorbance of the trityl ion at 335 nm. The consumption of the carbenium ion was recently shown to correspond quantitatively to the consumption of Si—H when an excess of the trityl salt was used [15], so initial and final absorbance may safely be correlated with concentrations. The rate constant was calculated from the last portion of the kinetic curve. Due to the low concentrations of reagents (10^{-4} mol dm^{-3}), the rate constant may be determined in this way by classical methods even for reactions having high rate constants (k up to 10^3 dm^3 mol^{-1} s^{-1}).

The reaction strictly obeys a second-order rate-law (first in silane and first in the total salt), even in the range in which free ions and ion pairs are present in

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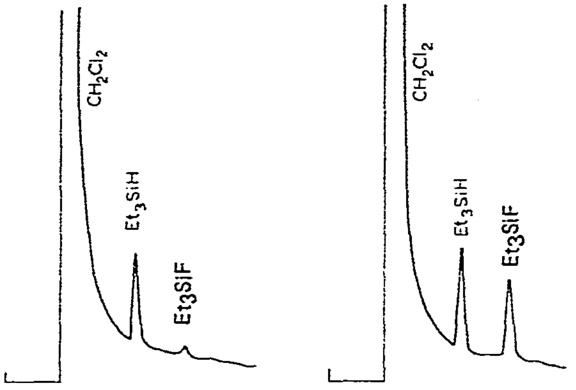
* Other complex anions like BF_6^- or $SbCl_6^-$ are less stable in solution [9].



Just after decoloration
(2 minutes)

a

after 13 minutes

b

Fig. 1. Gas-Chromatograms of the system containing initially $Ph_3C^+ SbF_6^-$ (2×10^{-3} mol dm^{-3}) and Et_3SiH (4×10^{-3} mol dm^{-3}) at 25°C: (a) sample injected just after decoloration indicating disappearance of Ph_3C^+; (b) sample injected after longer reaction time.

comparable concentrations. A series of runs involving a large excess of the silicon hydride was also performed. (Chloromethyl)dimethylsilane, which reacts relatively slowly, was used. Again the reaction showed good pseudo-first order kinetics over a large range of salt concentration. Attempts were made to relate the kinetic data to concentrations of free ions and ion pairs. The concentrations of these species in the reaction system were calculated using the value of equilibrium constant for ion-pair dissociation of $Ph_3C^+ SbF_6^-$ ($K = 1.6 \times 10^{-4}$ mol dm^{-3} at 25°C) given in ref. 14. As shown in Fig. 2 a constant value of k_{obs} was obtained only when the rate of disappearance of carbenium ion was correlated with the total amount of salt assuming equal reactivity of all carbenium species. Thus the reaction does not discriminate between free ions and ion pairs, as was further confirmed by experiments at different initial salt concentrations (Table 1). These results show clearly that the counter-ion SbF_6^- is not involved in the reaction in which the carbenium ion is removed.

Hydride transfer from triethylsilane to the trityl hexachloroantimonate $Ph_3C^+ SbCl_6^-$, was also studied. This salt is somewhat unstable in methylene chloride, and its decomposition products affect the kinetic results, which show a poor reproducibility (not better than ±40%). However to this precision the rate constant was the same as that for the reaction with trityl hexafluoroantimonate, confirming that complex anions have no significant role in the hydride transfer. In the absence of other nucleophiles able to neutralise the positive charge these results suggest that the hydride transfer may lead to formation of a silicocation species *. Additional support for this comes from the observation that the rate of reaction is little affected by the dielectric constant since the colour of the trityl ion disappeared at similar rates in mixtures of methylene chloride and n-heptane as in

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* Used here in the broad sense of any positively charged species containing a silicon atom bearing a considerable degree of positive charge.

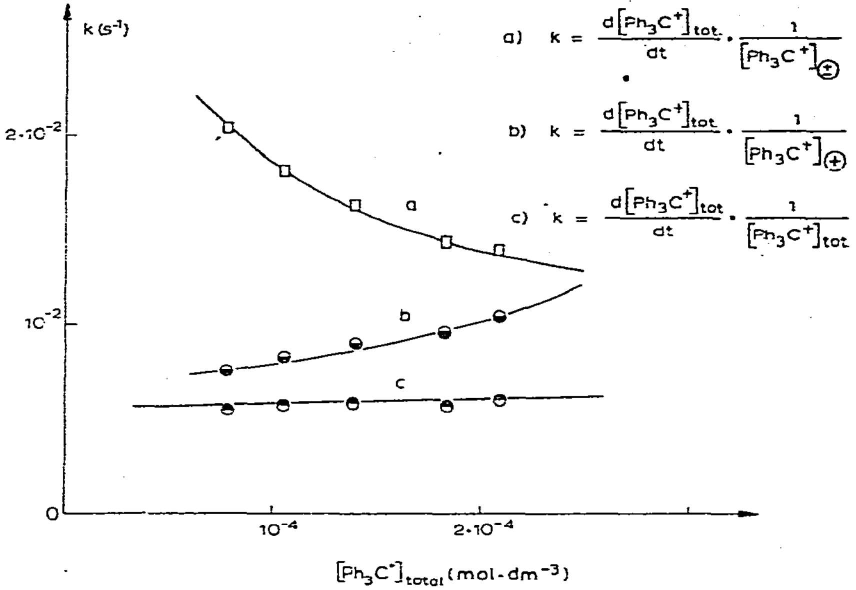

Fig. 2. The correlation of the pseudo first order rate constant with total salt concentration for the reaction of $(ClCH_2)(CH_3)_2SiH$ (4.83×10^{-3} mol dm^{-3}) with Ph_3C^+ SbF_6^- assuming that reactive species are: (a) ion pairs only; (b) free ions only; and (c) free ions and ion pairs showing equal reactivity.

pure methylene chloride. Reactions involving charge neutralisation are expected to be markedly accelerated in less polar media.

The silicocation intermediate would be very unstable. It was found that the electrical conductivity of the reaction mixture decreased in parallel with the consumption of carbenium ion, indicating that any silicocation must undergo fast transformation into an uncharged intermediate. Thus the over-all process of nucleophilic substitution of hydrogen at silicon is composed of at least three consecutive elementary reactions. The first, the hydride transfer, which is the most interesting, may be studied without interference from the other processes.

In deciding whether any other nucleophile might assist the silicocation formation, we had to take account of the fact that the reaction was studied at very low concentration of reactants (10^{-3}—10^{-5} *M*), and contaminants might appear in comparable or higher concentrations. To exclude possible participitation of contaminant nucleophiles, part of the CH_2Cl_2 was specially purified as described in ref. 16 *. The high purity of the solvent thus treated was confirmed by GLC analysis [16]. The kinetic results obtained using superpurified solvent were the same within experimental error as in the solvent purified in the ordinary way.

Most of the kinetic experiments were performed under prepurified nitrogen under conditions leading to the presence of about 10^{-3} *M* of water. This is about ten times as much as the amount of hydrosilane or trityl salt usually used. To

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* According to Cheradame et al. [16] this method is the only one which guaranteed the removal of contaminants from CH_2Cl_2 to the extent of giving reproducible kinetics in the cationic polymerization initiated by $TiCl_4$.

TABLE 1

THE SECOND ORDER RATE CONSTANT k_2 AND PSEUDO-FIRST ORDER RATE CONSTANT k_1 FOR HYDRIDE TRANSFER FROM $(ClCH_2)(CH_3)_2SiH$ TO TRITYL ION IN CH_2Cl_2 AT 25°C.

$[\equiv SiH]_0 \times 10^3$ (mol dm^{-3})	$[Ph_3C^+ SbF_6^-]$ $\times 10^4$ (mol dm^{-3})	$k_1 \times 10^3$ (s^{-1})	k_2 (dm^3 mol^{-1} s^{-1})	experimental procedure [a]
0.128	2.39	—	1.11	A
1.47	28.4	—	1.25	A
1.30	3.07	1.50	1.15	B
1.80	2.55	2.02	1.12	B
3.89	0.60	4.98	1.28	C
1.38	2.84	1.48	1.07	C
2.63	2.93	2.89	1.10	C
4.83	2.47	5.50	1.14	C
8.73	2.43	11.0	1.26	C
16.7	2.30	22.4	1.34	C

[a] Runs were performed as follows: A, under second order conditions, under nitrogen; B, under pseudo-first order conditions using high vacuum technique; C, under pseudo-first order conditions, under nitrogen.

rule out the possibility of water participation some experiments were performed using high vacuum techniques. The water present in the system was determined by Słomkowski and Penczek's method [12] based on the formation of colourless complexes between water and the trityl ion, the equilibrium of which is strongly shifted towards the complex at very low temperature (—80°C). In two independent experiments the water concentration was about 3×10^{-5} mol dm^{-3}, yet the rate was the same as in experiments in which the water concentration was about 100 times greater (Table 1). Moreover, since nucleophiles commonly form colourless complexes with the trityl ion at low temperature [11], the vacuum experiments also confirmed that other contaminants of nucleophilic strength comparable or higher than that of water do not play any appreciable role in the hydride transfer.

In one kinetic run some known amount of water (10^{-2} M) was deliberately introduced. It slowed down the hydride transfer to the extent which might be expected from known values of the equilibrium constant for the formation of the trityl—water complex. Similarly, introduction of appreciable amounts of HCl in one run did not affect the hydride transfer rate. It is also relevant to note here

TABLE 2

RATE CONSTANT FOR HYDRIDE TRANSFER TO THE TRIPHENYLMETHYLIUM CATION FOR VARIOUS HYDROSILANES IN CH_2Cl_2 WITH COUNTER ION SbF_6^- AT 25°C

Hydrosilane	k_2 [a] (dm^3 mol^{-1} sec^{-1})	Hydrosilane	k_2 (dm^3 mol^{-1} sec^{-1})
Me_3SiH	223	$(ClCH_2)Me_2SiH$	1.20
Me_2EtSiH	201	$PhMe_2SiH$	210
$MeEt_2SiH$	185	$(PrO)Me_2SiH$	199
Et_3SiH	139	$(Me_3SiO)Me_2SiH$	235
Et_3SiH [b]	120 ± 40	NpPhMeSiH	14.0
n-Pr_3SiH	175	$[Me_3SiO(Me_2SiO)_n]_2MeSiH$	24.1
n-Bu_3SiH	279	$(EtO)_3SiH$	0.15

[a] The reproducibility was normally better than ±10%. [b] Counter ion $SbCl_6^-$.

that the reproducibility of the kinetic results for most of the hydrosilanes studied was good. The data presented in Table 2 are mean values of series of several runs, and rate constants within a series were naturally reproducible to ±5%. All these results point to solvent molecules as the only species which may give nucleophilic assistance to the removal of hydride ion from silicon.

The effect of substituents at silicon on the reactivity in the hydride transfer was studied in order to obtain information about the structure of the intermediate formed in this reaction. The results indicate that the silicon atom carries an appreciable positive charge in the transition state. The introduction of a chlorine substituent in a methyl group of trimethylsilane decreases the rate by a factor of about two hundred, which corresponds to $\rho^* = -2.2$. However, the extent to which the electron-withdrawing inductive effect influences the reactivity is difficult to estimate, because electron-donating conjugation effects, the so-called α-effects [17] would tend to counter-balance the inductive effect and the true negative value of ρ^* may be larger. The important role of conjugation effects (especially, presumably $p_\pi - d_\pi$ conjugation) is manifested in the high reactivity of propoxydimethylsilane, pentamethyldisiloxane and phenyldimethylsilane (Table 2). The electron supplying conjugating effects of the substituents OPr, $OSiMe_3$, and Ph approximately counter-balance their electron-withdrawing inductive effects, because all these silanes react at about the same rate as trimethylsilane in yielding hydride ion to the trityl ion. Substitution of two or three methyl groups by alkoxy, siloxy, or aryl groups results in a pronounced decrease in reactivity, indicating that in those cases the inductive effect overwhelms conjugation effects. This is in agreement with the known phenomenon of saturation effects in $d_\pi - p_\pi$ interaction with increasing number of substituents capable of this type of interaction. The importance of the conjugation effects is additional evidence of a considerable partial positive charge on silicon in the transition state, which results in a contraction of the silicon d-orbitals and an increase in their ability to overlap with the p-orbitals of the substituents.

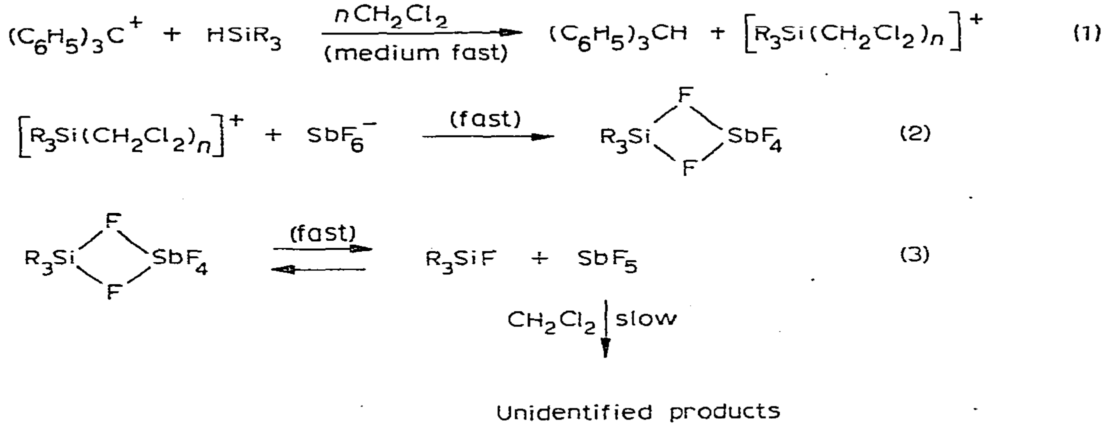
If the reaction leads to silicenium ion formation, no steric hindrance by substituents on silicon would be expected. However the reactivity was found to decrease with increase of n in the series $(CH_3)_{3-n}(C_2H_5)_nSiH$ (n = 0—3) (Table 2), indicating that steric hindrance slows the reaction down, in disagreement with an S_N1 mechanism. An interesting feature of the reaction is the non-regular change in the contribution of structural effects on changing the size of the substituents in the series of tri-n-alkylsilanes. The rate decreases on going from trimethyl- to triethyl-silane, but an increase in reactivity is observed on going to tri-n-propylsilane and to tri-n-butylsilane. This suggests some deeper change in the structure of the transition state with change in the size of alkyl substituents. In terms of the simplest mechanism involving silicenium ion it could be argued that there is a strong demand for the solvation of this kind of intermediate and the participation of solvent in the transition state is required. In the light of the ability of silicon to expand its valency, bidentate solvation by methylene chloride is feasible, or alternatively two solvent molecules could be ordinated. It is thus possible that in the case of smaller substituents the solvent molecules can take a position which more effectively stabilizes the transition state. The decrease of reactivity from Me_3SiH to Et_3SiH would thus reflect the decreasing effect of solvation on the structure of the transition state, while the increase in reactivity from Et_3SiH

to n-Bu_3SiH would indicate that if the structure of the transition state remains similar the inductive effect of substituents becomes more important. The question then arises, whether this type of intermediate, in which solvent molecules are considered to be ligands at silicon, can be called a silicenium ion. In any case other mechanistic pathways cannot be excluded *.

The structure of the second intermediate into which the silicocation is transformed is also unclear. According to Olah [18] fluorosilanes form pentacoordinate silicon complexes with SbF_5, and it seems probable that the second intermediate involves such a complex, which breaks down into fluorosilane and SbF_5 in the third step of the reaction.

However Olah observed a rapidly established equilibrium on the NMR time scale between the complex and free components, and thus we must assume that the third step involves an equilibrium lying over to the left, and that the complex breaks down as a result of the disappearance of free SbF_5, which is chemically unstable in CH_2Cl_2. The rate of disappearance of SbF_5 then determines the rate of formation of fluorosilane. The over-all reaction scheme would thus be as shown in Scheme 1.

SCHEME 1



Attempts were made to follow the kinetics of the third step for the reaction of n-Bu_3SiH, by GLC determination of the n-Bu_3SiF formed. The rate showed a complicated dependence on the initial concentrations of the initial reactants, trityl salt and n-Bu_3SiH. The reaction proceeded extremely slowly in the presence of a large excess of the salt. Presumably complexes of the type $SbF_5 \cdot SbF_6^-$ appear in the equilibrium 3, and the concentration of free SbF_5 is strongly reduced. On the other hand more than the stoichiometric amount of fluorosilane is produced (and correspondingly more hydrosilane disappears) in relation to the initial amount of salt when an excess of n-Bu_3SiH is used. This implies that SbF_5 or products of its decomposition can react under these conditions with hydrosilane. In the light of these complications the proposed scheme must be considered as offering only a simplified picture of the processes which follow the hydride transfer.

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* In some experiments at very low concentrations induction periods were observed. This may imply that the hydride transfer step is itself not an elementary reaction.

The results also point to possible complications in kinetic investigations of hydride transfer and in quantitative determination of $\equiv$Si—H groups (as described in ref. 9) by use of this reaction if the conditions enable the hydrosilane to react with products of processes which follow hydride transfer.

Experimental

Materials

Solvent. Reagent Grade methylene chloride was usually purified as described in ref. 19. The production of superpure methylene chloride (involving refluxing with 20% oleum, distillation, treatment with a phosphoric anhydride film and storage over and distillation from a sodium mirror was carried out as described in ref. 16. No impurity was detected by GLC in the CH_2Cl_2 thus purified.

Reagents. Dimethylpropoxysilane (b.p. 79.5°C) was obtained by propanolysis of dimethylchlorosilane in ether in the presence of triethylamine. It forms an azeotrope with propanol (b.p. 75.5°C, ca. 15—20% of propanol), and was purified by azeotropic distillation with benzene.

The other hydrosilanes used in the kinetic studies and the tri-n-butylfluorosilane used for GLC calibration are all known compounds. They were synthesised in standard ways and purified by distillation through a Perkin—Elmer 151 spinning band column. The purity as checked by GLC was usually better than 99.5%.

The Ph_3C^+ SbF_6^- (Alfa—Ventron) was purified as described in ref. 15. The Ph_3C^+ $SbCl_6^-$ was synthesized from Ph_3CCl and $SbCl_5$ and purified as in ref. 9.

Gas-chromatographic analysis

GLC analyses were made with a JEOL JGC 1100 Gas Chromatograph equipped with flame ionisation detector and a Takeda Riken 2215 A integrator. The conditions were usually as follows: 3 mm × 3 m stainless steel column filled with 10% dinonyl phthalate on Chromosorb WAW 60/80; temperatures: (Bu_3SiF analysis): column 100°C, injector 180°C, detector 200°C; the carrier gas was nitrogen at a flow rate of 60 ml/min. Tridecane was used as internal standard. In checking the purity of super-purified methylene chloride, 20% β,β'-oxydipropionitryle on Chromosorb WAW 60/80 was used at a column temperature of 60°C [16].

Kinetic measurements

Solutions of the trityl hexafluoroantimonate for kinetic studies (usual concentration 3×10^{-4} *M*) were made as previously described [9]. The solution was placed in a cylindrical vessel connected to a quartz optical cell L, closed with a teflon key stopcock (Fig. 3c). The vessel was placed in a thermostatted compartment of special design mounted on a Specord UV-VIS spectrometer. A known amount of the hydrosilane in methylene chloride was then introduced with a Hamilton hypodermic syringe. The cell was shaken and quickly returned to the compartment. The change of absorbance at 335 nm in time was recorded.

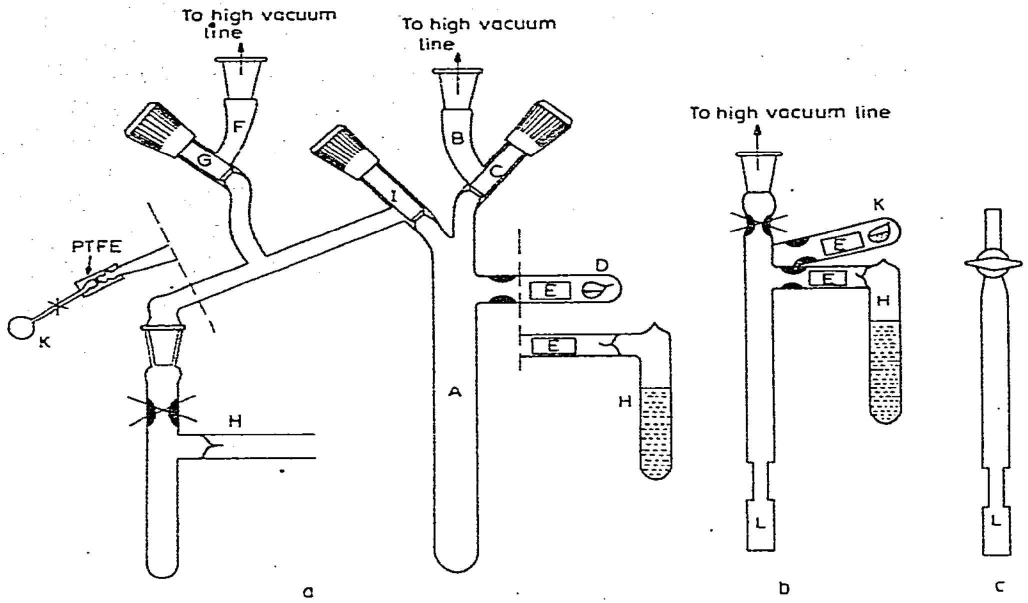

Fig. 3. (a) The apparatus for the preparation of the solutions for kinetic studies in high vacuum experiments, (b) the reactor for high vacuum kinetics experiments, and (c) the reactor used for normal kinetic experiments.

High vacuum kinetic experiment

The preparation of the solutions of trityl hexafluoroantimonate. The superpurified methylene chloride was kept over a sodium mirror in a vessel attached to the high vacuum line (hvl). The apparatus drawn in Fig. 3a was weighed and attached to the hvl by means of joint B. Part A was evacuated and carefully flamed (Rotaflo stopcock C-opened, I-closed) then immersed in liquid nitrogen. Methylene chloride was distilled in. The Rotaflo stopcock C was then closed and the apparatus removed from the hvl and weighed to determine the amount of CH_2Cl_2 introduced. The phial D containing a known amount of prepurified trityl hexafluoroantimonate was crushed by means of glass hammer E and the salt was dissolved in CH_2Cl_2. The apparatus was connected to hvl through the joint F and the remaining part of the apparatus, together with the weighed ampoule H, was evacuated and carefully flamed. Then stopcock G was closed and stopcock I opened. The ampoule was filled with the solution of the salt. Stopcock I was closed, then the ampoule H was immersed in liquid nitrogen and sealed at the constriction. It was weighed together with the joint to give the weight of the solution. The preparation of 3×10^{-4} mol dm^{-3} solutions for kinetic studies required a dilution, which was performed analogously in the same apparatus. The ampoule H was fused to the side arm of the vessel A as shown in Fig. 3a.

The preparation of the sample of hydrosilane. Prepurified chloromethyldimethylsilane was kept for at least one day over fresh calcium hydride, CaH_2, and was then distilled on the hvl into part A of the apparatus shown in Fig. 3a. It was then distilled into the weighed phial K which was connected to the apparatus by means of shrink-dealing teflon tubing. The phial was frozen in liquid nitrogen, sealed off and weighed together with the detached portion.

The determination of water content by Słomkowski and Penczek's method and kinetic runs. The ampoule with the solution of the trityl salt was fused through the breakseal to the reactor fitted with the quartz optical cell L (Fig. 3b) and the phial with the silane together with glass hammer were placed in a side arm of the reactor situated perpendicular to the ampoule containing the salt solution. The breakseal was crushed and the trityl salt solution transferred to the reactor. The reactor was placed in a Cryoson Technisch Lab CT 25R Dewar vessel fitted with TRL-3 temperature regulator. The Dewar vessel was mounted in a Unicam SP 1700 UV-Spectrometer. The spectra were taken in the range 350—600 nm at −72°C and again at 25°C. The water content was calculated as described in ref. 12 from the absorbances found at 335 nm at −72 and +25°C using the equilibrium constant $K_a = 2.0 \times 10^5$ for the colorless oxonium complex formation at −72°C, and a temperature coefficient of density of 1.8×10^{-3} g ml^{-1} deg^{-1}. The water content was found to be 3.4×10^{-5} mol dm^{-3}. The phial with hydrosilane was then crushed and the reaction was followed as described above.

In similar experiments, the water content was determined after mixing at −80°C of the salt solution and hydrosilane. The experiment showed that no substantial amount of water was introduced along with the hydrosilane.

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