JOURNAL OF CATALYSIS 11, 336–341 (1968)

Adsorption and Reaction of Methylchlorosilanes at an "Aerosil" Surface

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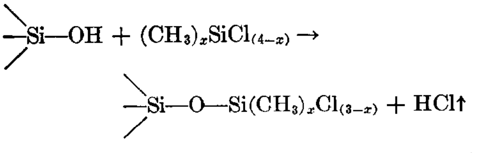
Received February 5, 1968; revised May 9, 1968

A gravimetric adsorption technique has been used to obtain quantitative data on the interactions of methylchlorosilane vapors with the hydroxyl groups of a silica surface.

Particular attention has been paid to the reactions which occur at elevated temperatures between surface hydroxyl groups and the vapors of mono-, di- and trimethylchlorosilanes. A rate equation consistent with the experimental data is derived and an activation energy calculated for each silane.

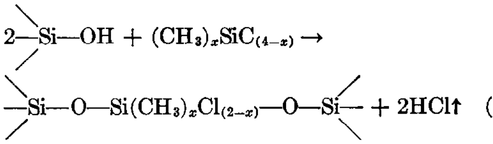
INTRODUCTION

The interaction of methylchlorosilanes with the hydroxyl groups of silica surfaces has been extensively studied using infrared absorption techniques (*1*). It has been shown that, at 30°C, the silanes are physically adsorbed at silica surfaces which have been preoutgassed at 450°C. At temperatures in excess of about 300°C irreversible adsorption occurs with the simultaneous elimination of hydroxyl groups from the surface. On the basis of this evidence a general equation may be written for the reaction of the methylchlorosilanes with surface hydroxyl groups at elevated temperatures.



$$\equiv\text{Si—OH} + (CH_3)_x\text{SiCl}_{(4-x)} \rightarrow \equiv\text{Si—O—Si}(CH_3)_x\text{Cl}_{(3-x)} + \text{HCl}\uparrow \quad (1)$$

When these reactions are followed by means of a quartz spiral spring balance it is immediately evident that the rates at which they proceed are strongly dependent upon temperature and vary greatly between the three silanes. Data has been obtained at a number of temperatures in the range 250–425°C and activation energies calculated for each silane. Consideration has been given to the fact that the activation energy might show a dependence upon surface coverage. Double elimination, according to Eq. (2). must be considered in the case of the dimethyl and monomethyl silanes



$$2\equiv\text{Si—OH} + (CH_3)_x\text{SiC}_{(4-x)} \rightarrow \equiv\text{Si—O—Si}(CH_3)_x\text{Cl}_{(2-x)}\text{—O—Si}\equiv + 2\text{HCl}\uparrow \quad (2)$$

This possibility is discussed in terms of the available experimental evidence.

EXPERIMENTAL

The adsorbent was an Aerosil silica having a surface area of 315 m^2g^{-1} as determined by BET analysis of nitrogen adsorption isotherms measured at 77°K.

Samples were prepared by pressing the powder into a disc 5 cm in diameter from which rectangular specimens of suitable size were cut. The thickness of the specimens varied between 0.15 and 0.20 mm.

The silica plates were pretreated in an identical manner before each experiment by heating in air at 500°C for 1 hr followed by evacuation at 450°C for a similar period.

A conventional quartz spring balance

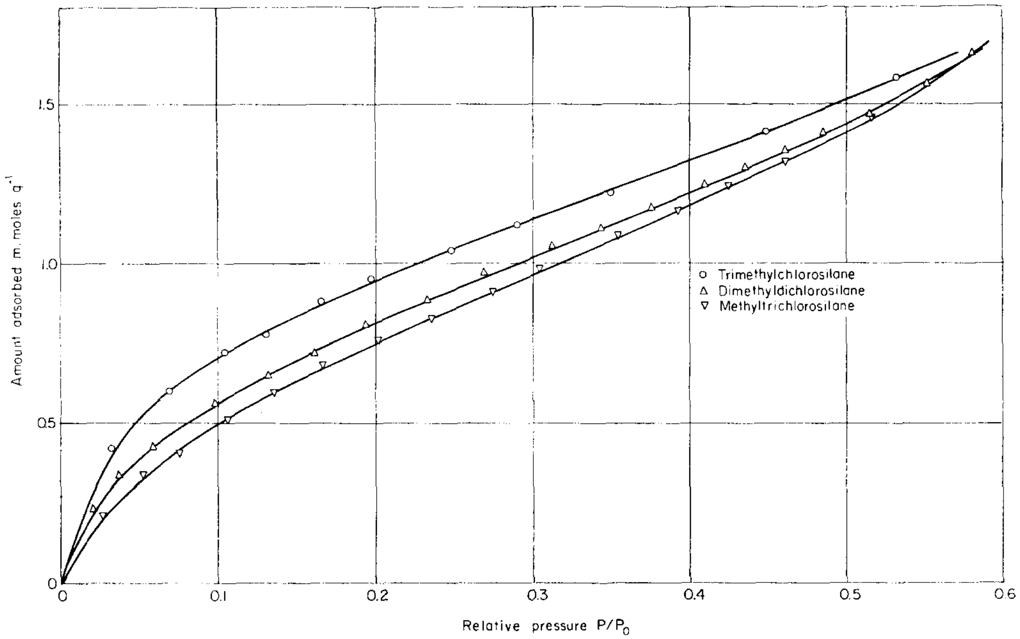


FIG. 1. Adsorption of methylchlorosilanes on Aerosil at 30°C.

was used for the kinetic measurements and, with slight modification, the same apparatus was used for the measurement of adsorption isotherms at 30°C and for the determination of surface area by nitrogen adsorption at 77°K.

Kinetic measurements were made over the range of temperature 250–425°C in which the reactions proceeded at a convenient rate. All measurements were made at a constant silane pressure of 2.3 cm Hg and in all cases the volume of silane (about 5 liters) in contact with the sample was sufficiently large to justify the assumption that the silane pressure remained constant at this value during the course of each experiment.

The silanes were outgassed and freshly distilled under vacuum before each run.

RESULTS

A. *The Adsorption of Methylchlorosilanes on Aerosil at 30°C*

Infrared absorption measurements have shown (*1*) that the methylchlorosilanes adsorb physically at Aerosil surfaces which have been pretreated under vacuum at 450°C. Absorption in the spectrum at 2.67 μ, which is typical of isolated (i.e., non-hydrogen-bonded) surface hydroxyl groups, is displaced but not eliminated as the silanes are adsorbed.

The gravimetric data are in full agreement with these observations and the adsorption isotherms shown in Fig. 1 are completely reversible. Table 1 shows the silane monolayers derived by application of the BET equation to these isotherms. These suggest that the surface can accommodate approximately 1.7 physically adsorbed silane molecules per 100 Å^2.

TABLE 1
PHYSICAL ADSORPTION DATA FOR METHYLCHLOROSILANES ADSORBED ON AEROSIL SILICA AT 30°C AFTER OUTGASSING AT 450°C

	BET monolayers		Apparent molecular areas
Silane	Mg g^{-1}	Molecules/ 100 Å^2	(Å^2)
$(CH_3)_3SiCl$	97	1.70	58.6
$(CH_3)_2SiCl_2$	111	1.64	60.8
$(CH_3)SiCl_3$	128	1.63	61.2

If it is assumed that a reacted silane

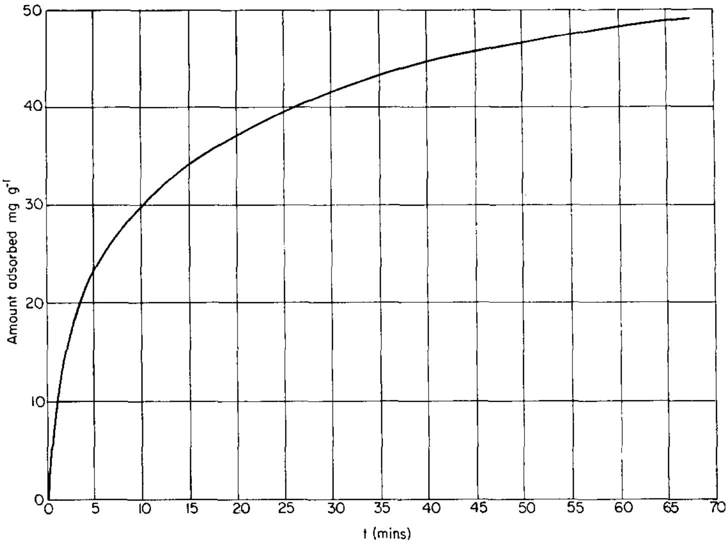


FIG. 2. Plot of total amount adsorbed as a function of time for the reaction between trimethylchlorosilane and Aerosil at 425°C.

residue will occupy approximately the same area as the physically adsorbed silane molecule then, at a surface containing greater than about 1.7 -OH groups per 100 Å^2, reaction will be controlled by steric effects which will limit silane uptake to 1.7 reactions per 100 Å^2. At a surface containing less than 1.7 -OH groups per 100 Å^2 silane uptake will be limited by the number of available -OH groups and will then be a reliable measure of hydroxyl population at that surface.

B. *The Reaction of Methylchlorosilanes with Aerosil Silica at Elevated Temperatures*

At temperatures in excess of about 250–300°C reactions occur between the surface hydroxyl groups of Aerosil and methylchlorosilane vapors according to Eq. (1), (*1, 2, 3*). Hydroxyl absorption in the infrared at 2.67 μ is now completely eliminated and bands due to -CH stretching frequencies appear. The reaction product is extremely stable and may be heated to 500°C in vacuum or 400°C in air without serious loss of organic material.

The reaction rates are extremely dependent upon temperature and decrease rapidly as the surface becomes progressively covered with reacted silane residues. Figure 2 shows a typical relationship between the total amount of silane adsorbed and total time. At any temperature the three silanes show the same general behavior but react at very different rates. This is illustrated in Fig. 3 where the fractional reaction coordinate for each silane is plotted as a function of time for a reaction temperature of 325°C. In all cases reaction ceases when hydroxyl groups have been totally eliminated from the surface. This is indicated by the complete disappearance of hydroxyl absorption in the infrared and by the fact that final uptakes are always less than those estimated for a sterically limited reaction. The data obtained for trimethylchlorosilane were analyzed in greatest detail since it is only for this silane that complications due to possible double elimination may be discounted. The reaction may be represented by an equation of the form

$$dq/dt = KF(q)\exp(-E_a/RT) \qquad (3)$$

where

$$q = \frac{\text{Weight of silane adsorbed at time } t}{\text{Weight of silane adsorbed at completion of reaction}}$$

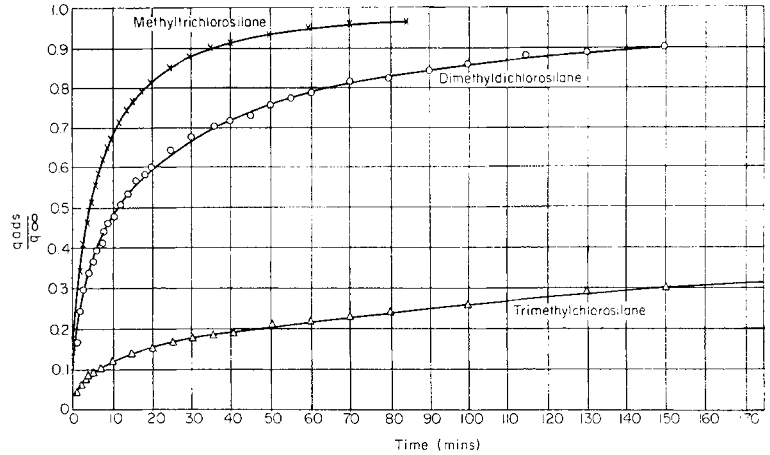


FIG. 3. Plots of q_{ads}/q_∞ as a function of time for the reaction between methylchlorosilanes and Aerosil at 325°C.

and $F(q)$ is a complex function of q, essentially temperature-independent.

Calculation of activation energies at a number of values of q in the range $q = 0.25$–0.58 showed E_a to be independent of q within the experimental limits. Mean activation energies were therefore calculated from the experimental data using the integrated form of Eq. (1). Plots of log $t_{1/2}$ vs. $1/T$, where $t_{1/2}$ is the half-time of the reaction, have slopes equal to $E_a/2.3R$. Figure 4 shows these plots for the three silanes and activation energies calculated from these are listed in Table 2.

The lower activation energies observed for the dimethyl and monomethyl silanes may be significant but the possibility of secondary reaction in these cases make it difficult to draw a direct comparison with the trimethyl compound. The dimethyl and monomethyl silanes also show anomalous behavior in terms of the final maximum uptake recorded at completion of the re-

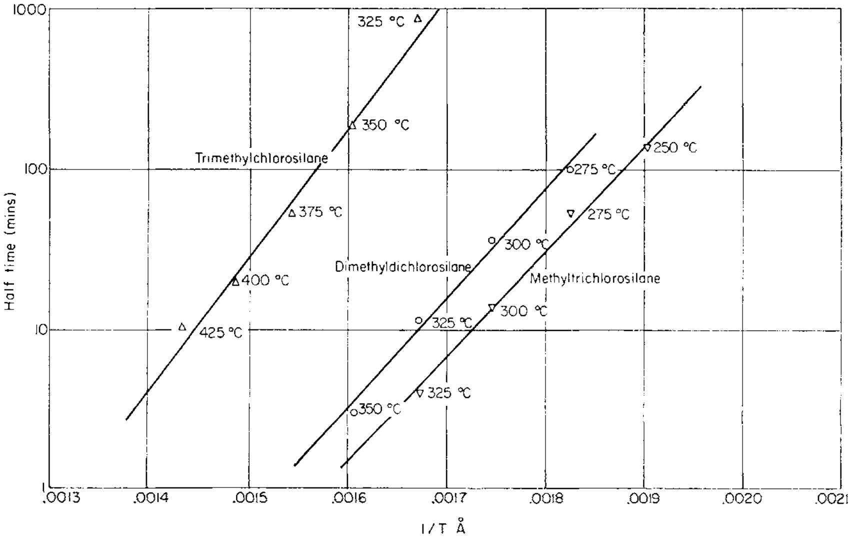


FIG. 4. Plots of log $t_{1/2}$ vs. the reciprocal of the absolute temperature for the reactions between methylchlorosilanes and Aerosil.

TABLE 2
ACTIVATION ENERGIES FOR THE REACTION BETWEEN METHYLCHLOROSILANES AND AEROSIL AT ELEVATED TEMPERATURES

Silane	Mean activation energy ±3 kcal mole^{-1}	Temperature range (°C)
$(CH_3)_3SiCl$	37	325–425
$(CH_3)_2SiCl_2$	31	275–350
$(CH_3)SiCl_3$	30	250–325

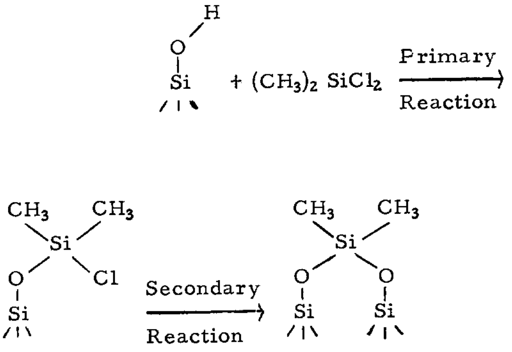
action. Data for the three silanes are collected in Table 3.

Thus the hydroxyl populations calculated from the uptake of the dimethyl and monomethyl silanes, assuming a 1:1 reaction ratio, are 1.26 and 1.20 –OH groups per 100 Å^2, respectively, in good agreement with those reported for a rehydrated Aerosil silica outgassed at 500°C (*2*), whereas that calculated from the uptake of the trimethyl silane is 1.59 –OH groups per 100 Å^2. The physical adsorption data suggest that little difference exists in molecular size between the three silanes and that the surface can accommodate 1.6 or 1.7 silane molecules per 100 Å^2. The low uptakes of the dimethyl and monomethyl silanes cannot therefore be explained on the basis of steric effects. Since only one reaction is possible for the trimethyl silane, it can be assumed that the uptake of this is a reliable measure of hydroxyl population and, in order to explain the experimental data, some degree of double elimination must be assumed for the dimethyl and monomethyl silanes. The results are consistent with a reaction mechanism in which the percentages of surface hydroxyl groups reacting doubly with the dimethyl and monomethyl silanes are about 31% and 39%, respectively.

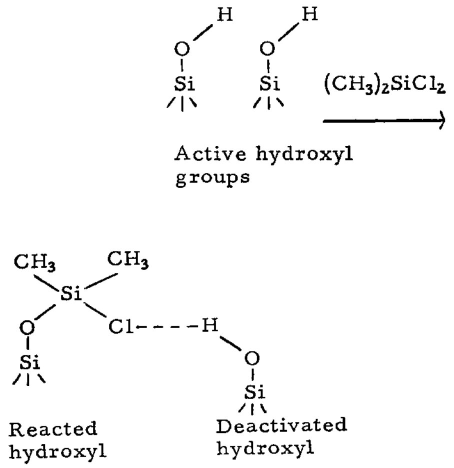
TABLE 3
UPTAKES OF METHYLCHLOROSILANES ON AEROSIL AT ELEVATED TEMPERATURES

Silane	Observed uptake (mg/g of silica)	Hydroxyl population assuming 1:1 reaction (–OH groups per 100 Å^2)	Number of silane molecules accommodated per 100 Å^2 (from physical adsorption data)
$(CH_3)_3SiCl$	60	1.59	1.70
$(CH_3)_2SiCl_2$	61	1.26	1.64
$(CH_3)SiCl_3$	71	1.20	1.63

Certain geometric requirements must be met if a silane is to react on a 1:2 basis with surface hydroxyl groups and, ideally, the pair of hydroxyls involved should be separated by a distance of about 3 Å. This is considerably less than the separation expected after outgassing the silica at 450°C and some mobility of surface hydroxyl groups must be assumed. The reaction mechanism would then involve an initial reaction of the silane on a 1:1 basis followed by the possibility of a secondary process involving the elimination of a second molecule of HCl.



Alternatively it may be argued that the low final uptakes observed for the dimethyl and monomethyl silanes may be explained in terms of deactivation of surface hydroxyl groups by adjacent, reacted silane residues without actual elimination of HCl.



Such a mechanism would, however, require that a considerable number (about 20%) of hydroxyl groups remain on the surface on completion of the reaction and these would be expected to show an absorption band in the infrared. Our data would not support this since residual absorption at 2.72 μ is present for all three silanes and is due not to unreacted surface hydroxyl but to internal hydroxyl which is unavailable for reaction.

CONCLUSIONS

(1) Gravimetric adsorption measurements confirm that adsorption of methylchlorosilanes at surface hydroxyl sites is physical and reversible at 30°C. Molecular areas are 59, 61, and 61 $Å^2$ for the physically adsorbed trimethyl, dimethyl, and monomethyl silanes, respectively.

(2) At temperatures in excess of about 250°C hydroxyl groups react with the methylchlorosilanes at rates which are strongly dependent upon temperature and which, at any temperature, decrease rapidly as the reactions go to completion.

(3) At any temperature reaction rates are in the order

$$(CH_3)SiCl_3 > (CH_3)_2SiCl_2 \gg (CH_3)_3SiCl$$

(4) Activation energies are independent of surface coverage within the limits of experimental accuracy. Values are 37, 31, and 30 kcal $mole^{-1} \pm 3$ kcal $mole^{-1}$ for trimethyl, dimethyl, and monomethyl silanes, respectively.

(5) Uptakes of the dimethyl and monomethyl silanes are consistent with a mechanism which results in approximately 31% and 39% of the available surface hydroxyl reacting on a 2:1 basis with dimethyl and monomethyl silane, respectively.

ACKNOWLEDGMENTS

The authors wish to thank the directors of Pilkington Brothers Ltd. for permission to publish this paper and to acknowledge the assistance of Mrs. D. M. Henderson during the course of the work.

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