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The kinetics of silylation of hydroxylated silica
1: Aerosil

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Abstract: The kinetics of the silylation of hydroxylated silica, the non-porous Aerosil using trimethylchlorosilane, under various reaction conditions has been investigated by a gravimetric technique and found to follow the law:

$$\left[\frac{1+b}{t}\right]\ln\left\{\frac{M_\infty}{M_\infty - M_t}\right\} - \frac{M_t b}{M_\infty t} = k_a$$

which represents a first order reaction retarded by one of its products. From this analysis, the activation energy in the temperature range 598 K to 673 K, was found to be 155 kJ mol^{-1}. The reaction is independent of pressure at values greater than 15 torr.

Key words: Aerosil – silylation kinetics – trimethylchlorosilane

Introduction

The silylation of silica, and many other hydroxylated adsorbents, has been used in the determination of the population of hydroxyl groups on the surfaces of the adsorbents. The resulting surfaces are hydrophobic, and show marked reduction in adsorption particularly of electron donor molecules. Because of their selective adsorption properties, these modified adsorbents are finding increasing applications in the field of chromatography, in industry and in reducing the fragility of optical fibres. A detailed study of the kinetics of silylation should reveal the mechanism and the optimum reaction conditions.

The kinetics of the silylation reaction depend, among other things, on the silane used [1, 2, 3], and on the type of silanol groups at the surface [4, 5, 6, 7, 8]. However, the mechanism of silylation using halosilanes is not yet clearly understood. In this case, the reaction is characterised by a fast initial part followed by a subsequent slow process. The fast reaction was attributed to "very active hydrogen bonded silanol groups" by Snyder and Ward [4], to part replacement of silanols by Chlorine atoms by Hertl and Hair [5], and to geminal and vicinal silanols by Van Venzelen [6]. The slow process was attributed to isolated silanol groups by some workers [4, 6], and to steric hindrance by others [2].

Chlorinated silanes are physisorbed around 303 K but chemisorbed at and above 523 K [7]. Under optimum reaction conditions, TMCS selectively reacts with isolated silanols on a one-to-one ratio in a first order reaction [7].

Attempts to fit the entire range of experimental data to a suitable rate law have not been quite successful. However, in the derivation of the kinetic law; the adsorption of the side products such as the halo acids (HX), has not been considered. These are likely to complicate the kinetics particularly when the gravimetric technique is used.

This paper provides the data for analysis, reviews the various analytical methods which have been used and investigates the unexplored possibility of the retardation of the reaction by the adsorption of HX.

Experimental

Apparatus and materials

A schematic diagram of the apparatus which was used for all the silylation reactions is given in Fig. 1. A mercury diffusion pump, backed by a rotary pump is used to achieve a vacuum of about 10^{-5} torr, as checked with a McLeod gauge. The pressure in the system is followed using a calibrated pressure transducer (PT), the output of which is in units of mV. The output is assumed to remain linear, with respect to pressure in the pressure range 0 to 760 torr, 1 mV being approximately equivalent to 4.615 torr.

The silica sample used was Aerosil crush obtained from pellets prepared in a hand press. It was chosen because it is a nonporous silica sample. This was to minimise mass transfer problems which complicate the study of a porous sample.

Trimethylchlorosilane (TMCS) of BDH Chemicals Ltd of Poole and of purity 99.99% was chosen as the organosilane for the study. This was transferred directly to the sample reservoir and purified by the freeze-thaw process.

The extent of the silylation reaction was followed gravimetrically using a vacuum electronic microbalance, connected to the vacuum frame using a brass flange and flexible metal bellows, (C.I. Electronics, Salisbury). Details of the balance and its mode of operation have been described in detail elsewhere [18].

Table 1. Conditions of reaction for the silylation of silica (all Temp K)

Run no	*T* pretreat	*T* react	extent
1(× 2)	598	598	infinity
3(× 3)	673	673	infinity
4(× 3)	673	663	infinity
5(× 3)	653	653	infinity
7(× 4) *)	673	653	infinity
9(× 2)	673	598	inf.,1/4

*) experiments performed at different pressures to check on the effect of pressure changes for pressures > 15 torr.

Procedure

A sample of Aerosil, of mass about 200 mg, was loaded into a silica sample bucket and suspended from the microbalance. The balance had been calibrated prior to loading.

The system was pumped out at room temperature for 24 hours, by which time the samples had reached a constant weight. The stability of the vacuum was tested by isolating the system from the pumps for several hours and checking for leaks.

The adsorption line to tap 2 was flushed several times with oxygen, using tap 1 (see Fig. 1). An oxygen pressure of approximately 100 torr was then let into the system, between tap 1 and 2 (with tap 3 open), and the temperature of the sample raised to 473 K for several hours to oxidise any organic contaminants.

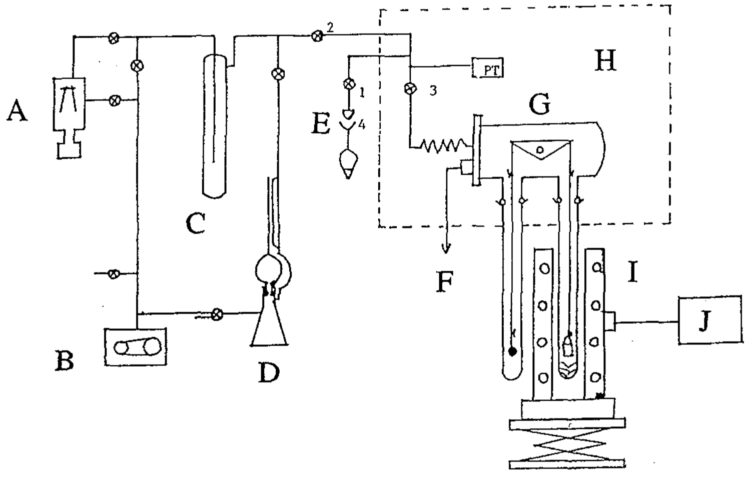


Fig. 1. The apparatus used for the study of the kinetics of silylation of hydroxylated silica. A Mercury diffusion pump, B Rotary pump, C Cold trap, D McLeod gauge, E Silane sample bottle or inlet for oxygen, F Voltage output, G Microforce balance, H Air Thermostat, I Furnace, J Electronic control unit

The sample was re-evacuated at the required pretreatment temperature for 2 to 3 hours to dehydroxylate the surface, rehydroxylated at a water vapour pressure of 10 torr for twelve hours at the reaction temperature, then evacuated for half an hour to eliminate residual water vapour, and then silylated using a predetermined excess vapour pressure of the silane to ensure that the pressure remained constant throughout the duration of the reaction. An air thermostat together with heat tapes on the exposed parts of the reaction vessel were also used in maintaining a constant vapour pressure of the reactant when necessary. The reaction was followed gravimetrically, with the mass being recorded by the chart recorder connected to the electronic microbalance, as a function of time.

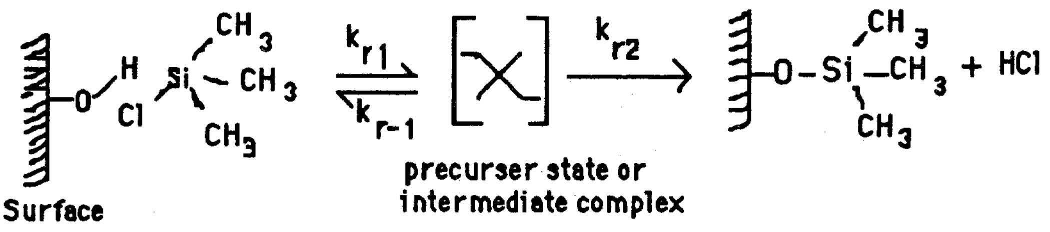
When the reaction had progressed to the desired extent, the reaction temperature was raised to and maintained at 673 K for about two hours to ensure the reaction was complete or to check that there was little further change. The reaction could also be stopped as desired by cooling and pumping out the residual vapour through a liquid nitrogen cold trap. The sample weight at the end of the reaction was recorded and the mass gained was obtained by difference.

Results and discussion

In this section, results of the chemisorption of TMCS by Aerosil are presented. This is done by presenting three models and testing them on the results. The most appropriate model for the analysis of the experimental results is then identified. In all cases, a line fitting program based on the least squares analysis was used. The algorithm of the programme was periodically altered to suit each type of model.

The chemical reaction model

In this model [19], the participation of a precursor state is assumed. The precursor state is considered to be a short-lived intermediate complex. Therefore, the stationary state approximation can be applied to it. Our reaction scheme using this model is given below:



In this study, poor mass transfer to the surface was minimised by using a large volume of the appropriete silane (2.5 dm^3) and by keeping the silane pressure as high as possible. The concentration of the silane at the surface can be considered to have remained constant throughout the reaction. Therefore, the rate of chemisorption (equivalent to the rate of increase in mass M of the adsorbent) should be proportional to the concentration of the intermediate complex $[\chi]$ which is itself proportional to the concentration of the surface silanols:

$$\frac{dM}{dt} = k_{r2}[\chi] \qquad [1]$$

If we assume that a steady state has been established, then

$$\frac{d[\chi]}{dt} = 0 = k_{r1}\,[\mathrm{OH}] - k_{r-1}[\chi] - k_{r2}[\chi] \qquad [2]$$

$$[\chi] = \frac{k_{r1}[\mathrm{OH}]}{(k_{r-1} + k_{r2})} \qquad [3]$$

[OH] may be represented by coverage per unit area θ_{OH}

$$\theta_{\mathrm{OH}} = (1 - \theta_r) = \left(1 - \frac{M}{M_\infty}\right) \qquad [4]$$

where $\theta_r = M/M_\infty$ is the coverage of the silane and M_∞ is mass gain when the reaction is complete. If we put

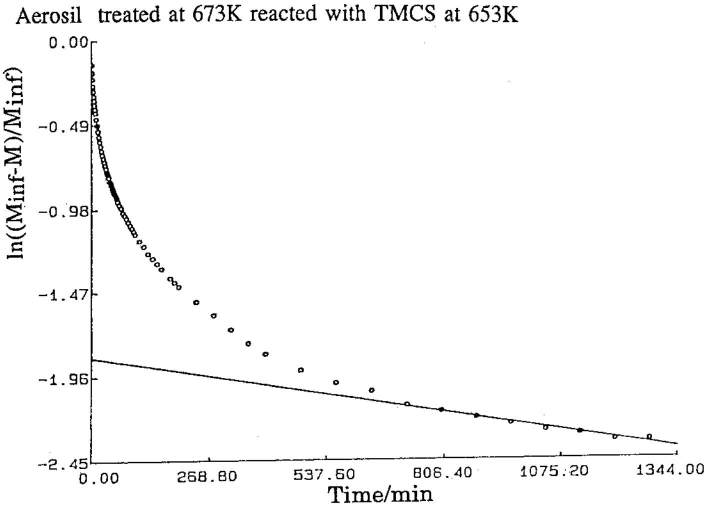


Fig. 2. A plot of 1st order integrated equation the chemical reaction model for the chemisorption of TMCS at 653 K on Aerosil pretreated at 673 K. (the first straight line plot is shown)

$$k = \frac{k_{r2}k_{r1}}{(k_{r-1} + k_{r2})}$$

$$\Rightarrow \frac{dM}{dt} = k\,[\mathrm{OH}] = k\theta_{\mathrm{OH}} = k\left\{1 - \frac{M}{M_\infty}\right\} \qquad [5]$$

which on integration yields an equation similar to that derived by Ritche (11):

$$\ln\left\{\frac{(M_\infty - M)}{M_\infty}\right\} = -kt \qquad [6]$$

M_∞ (here after labelled $M_{\infty 1}$ to distinguish it from other reactions) is the final mass at the end of the reaction. A plot of $\ln[(M_{\infty 1} - M)/M_{\infty 1}]$ against time t should be linear. A sample plot is given in Fig. 2. (run 7).

As can be seen in the above plot, a curve is obtained instead of a straight line. However, after about 80% of the reaction, the plot is linear.

One method of analysing such data is as follows:

If it is assumed that for this result, either several reactions were taking place concurrently or consecutively, in which case the linear part of the curve can be assumed to represent the slowest of the reactions; or if the surface is heterogeneous, then the linear part of the curve can be assumed to represent the least reactive group of surface silanol groups. (The intercept at $t = 0$ gives the corresponding values of $M_{\infty 2}$, the final part of the reaction represented by the first straight line; and

$$M_{\infty 3} = M_{\infty 1} - M_{\infty 2} \qquad [8]$$

At every experimental point, the value of the mass corresponding to the linear portion is subtracted from the value on the original curve. The resulting mass difference ΔM, is given by:

$$\Delta M = M_\infty\,\{\exp(\text{orig. curve value}) - \exp(\text{line value})\} \qquad [7]$$

Masses obtained this way are again used for another plot of $\ln(\Delta M/M_{\infty 3})$ against t. This subtraction process may be continued until all data are covered.

In the greatest number of cases, three straight lines plots were obtained (as in the case of Figs. 2, 3 and 4). In a minority of cases 4, and in one case only 2, lines were observed. Furthermore, the position of these lines is fixed by trial and error. The resulting rate constants will therefore vary. This method proved to be unreliable and could not be used.

Hertl and Hair [5, 3], and Evans and White [7] have found chemisorption of TMCS to follow simple 1st order kinetics. Hair and Hertl followed the reaction by measuring the intensity of the peak of absorption of the surface silanols in the infrared region of the spectrum for about four hours. However, their data represent only about 80% of the reaction. Evans and White followed the reaction gravimetrically for a similar period, and analysed the data using the halflife period procedure obtaining a higher activation energy than that obtained by Hair and Hertl [5, 3]. The higher value is thought to represent both the slow and fast reaction.

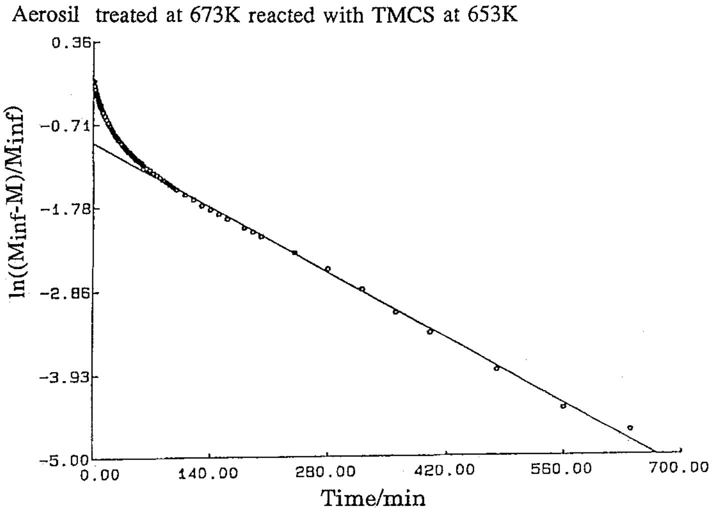


Fig. 3. A plot showing the 2^{nd} straight line for the 1st order integrated equation from the chemical reaction model for the chemisorption of TMCS at 653 K on Aerosil pretreated at 673 K. after the subtraction of the slowest reaction (values of the first straight line from figure 2).

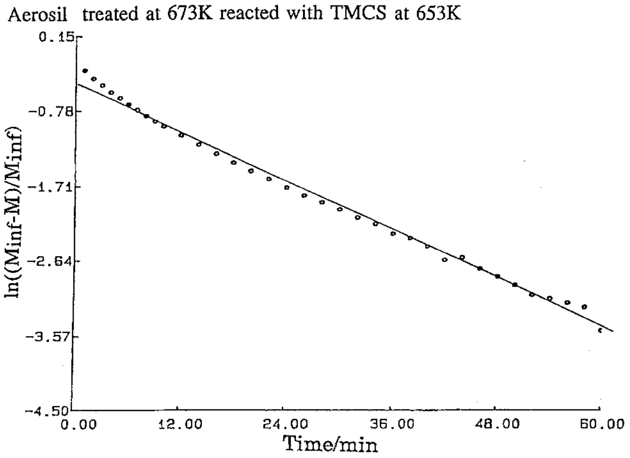


Fig. 4. A plot of the 3rd straight line for the 1st order integrated equation from the chemical reaction model for the chemisorption of TMCS at 653 K on Aerosil pretreated at 673 K. after subtraction of the two slower reaction

The Elovich model

The second model is also based on Langmuir's model of activated adsorption on a heterogeneous surface, but does not involve a precursor state in the analysis. This results in another form of the logarithmic rate law, known popularly as the Elovich equation (20). The integrated form of the equation used relates the mass q adsorbed at any time t by:

$$q = \mathrm{A} + \mathrm{B}\{\ln(t + t_0)\} \qquad [8b]$$

where $t_0 = \mathrm{A}$, A and B are constants, and $q = q_0$ at $t = 0$.

A plot of the quantity adsorbed, q, against $\ln(t + t_0)$, where t_0 is regarded as an adjustable constant, can be made to give a straight line.

A sample of the resulting plots is given in figure 5 for the chemisorption of TMCS on Aerosil (run 7).

For all samples, the plots had breaks, and in most cases were convex to the time axis. According to Low [9], the plot is convex to the time axis if there is a large instantaneous adsorption; and the breaks represent changes in the reaction mechanism. However, Gulsuzka [10] and Ritche [11] have shown that in many cases, this is not correct. Manipulation of the plot by changing the value of t_0 to obtain linearity has been used by

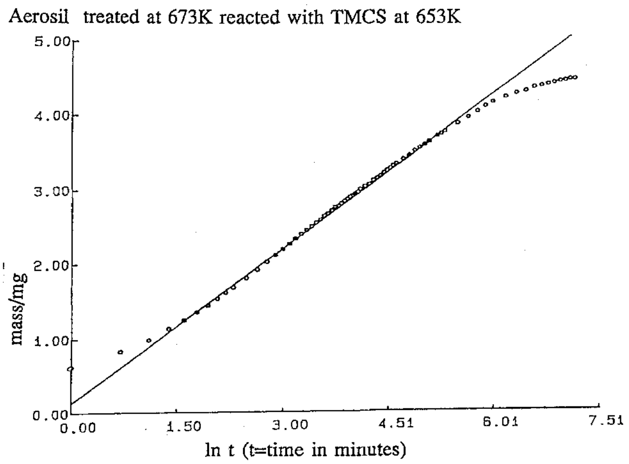


Fig. 5. A test of the Elovich model for chemisorption of TMCS at 653 K on Aerosil pretreated at 673 K

many workers [5, 7, 12]. There is, however, no plausible justification for the use of this. In the presence of reasonable alternatives, it is probably wiser to avoid the method.

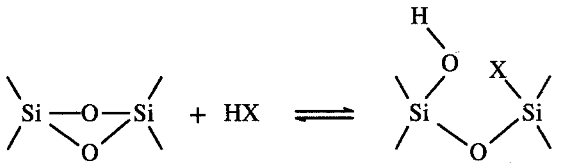
It was claimed that a test reaction showed that hydrogen chloride, a product of the silylation reaction, did not react with silica at elevated temperatures [7]. However, analysis of the silylated silica has revealed the presence of chemisorbed chlorine at the surface [5, 7]. Furthermore, recent authors seem to believe that hydrogen chloride interacts with silanol groups [13], and in so doing probably retards the silylation reaction. This leads to the third model used to analyse the data obtained in the present work.

The model based on retardation of reaction by HX

The homogeneous reaction between hydroxylated compounds and halosilanes, in solution, is instantaneous, and the energy of activation is very small [14]. The heterogeneous reaction between a halosilane vapour and the silanols at the surface of a solid should also be fast, under similar conditions. The initial stages of the heterogeneous reaction, particularly with the smaller halosilane molecules, conform to our expectation of high rate. Subsequently, however, the slow process, which may continue for weeks, takes over. Since chlorine, chemisorbed on the surface during silylation with TMCS, has been detected and quantified [5, 7], the slowing down of the reaction may be attributed to the presence of the halo acids (HX = HCl) at the surface.

In order to test the effect of HCl on the silylation of Aerosil using TECS, a reaction which had practically halted was stopped completely by pumping off the reaction mixture. When an equivalent pressure of fresh TECS was introduced, the reaction resumed with a higher rate than that at the time of the pumping off of the silane. This showed that the slowing down of the reaction was related to the presence of the vapours in the reaction mixture. The only other vapour present in this case, and thus the poison to the reaction of interest, was HCl.

Either the halo acid produced in the silylation reaction slowly chemisorbs across the strained surface siloxane bond in an equilibrium reaction producing more silanols thus:



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or the halo acid competes, through hydrogen bonding, with the silane molecules for the adsorption sites (the silanols), thus slowing down the silylation reaction. In both cases, the chlorine at the surface creates a steric barrier to easy chemisorption of silanes.

Therefore, the reaction can be considered as a unimolecular reaction retarded by one of its products. If the coverage by the silane is θ and the corresponding partial pressure is P, and if the coverage by the adsorbed poison (HX) is θ' and its corresponding partial pressure is P', the fraction of sites which are free is then $(1 - \theta - \theta')$. The rate of adsorption of the silane would thus be

$$\frac{d\theta}{dt} = k_a P(1 - \theta - \theta') \qquad [10]$$

If adsorption equilibrium is attained then

$$k_a P(1 - \theta - \theta') = k_d \theta \qquad [10a]$$

Since the pressure of the silane was kept high it can be assumed to have remained constant. Therefore we can put

$$K = P\frac{k_a}{k_d} \qquad [10b]$$

$$\Rightarrow \theta = \frac{K(1 - \theta'')}{K + 1} \qquad [10c]$$

if we put $K_1 = K/(K + 1)$ then

$$\theta = K_1(1 - \theta'') \qquad [10d]$$

Similarly, the rate of adsorption of the poison (HX) is:

$$\frac{d\theta'}{dt} = k'_a P'(1 - \theta - \theta') \qquad [11]$$

The rate of desorption of the poison is $k_d'\theta'$ [12]

If adsorption equilibrium is attained by the poison, then:

$$k_a'P'(1-\theta-\theta') = k_d'\theta' \qquad [13]$$

substituting for θ in equation [13] using equation [10d] and solving for θ' leads to the isotherm

$$\theta' = \left\{\frac{(K'-K'K_1)P'}{1+(K'-K'K_1)P'}\right\} \qquad [14]$$

where

$$K' = \frac{k_a'}{k_d'}$$

The pressure of the poison P' is related to θ by the stoichiometric equation:

$$(\mathrm{Me})_3\mathrm{SiCl} + \mathrm{Site} \rightarrow (\mathrm{Me})_3\text{–}\mathrm{Si}\text{–}\mathrm{Site} + \mathrm{HCl} \qquad [15]$$

$$\Rightarrow P' = K''\theta \qquad [16]$$

$$\Rightarrow \theta' = \left\{\frac{(K'-K'K_1)K''\theta}{1+(K'-K'K_1)K''\theta}\right\} \qquad [17]$$

if we put $b = (K'-K'K_1)K''$

$$\theta' = \frac{b\theta}{1+b\theta} \qquad [18]$$

This isotherm is then substituted in the rate equation for the chemisorption of silanes:

If we put $k_{a1} = k_aP$

$$\frac{d\theta}{dt} = k_{a1}\left\{1-\theta-\left(\frac{b\theta}{1+b\theta}\right)\right\}$$

$$\frac{d\theta}{dt} = \frac{k_{a1}}{(1+b\theta)}\{1-\theta-b\theta^2\}$$

The term $b\theta^2$ can be ignored because it is very small.

$$\frac{d\theta}{dt} = k_{a1}\left\{\frac{1-\theta}{1+b\theta}\right\} \qquad [19]$$

$$\int\left\{\frac{1+b\theta}{1-\theta}\right\}d\theta = \int k_{a1}dt$$

$$-(1+b)\ln(1-\theta) - b\theta = k_{a1}t \qquad [20a]$$

This equation can be transformed into an equation involving masses adsorbed on the surface. If M_∞ is the final mass of the adsorbed silane per unit area and M_t is the mass adsorbed at any time t, the coverage θ is given by M_t/M_∞. The rate of reaction, with retardation, is then:

$$\left[\frac{1+b}{t}\right]\ln\left\{\frac{M_\infty}{M_\infty - M_t}\right\} - \frac{M_tb}{M_\infty t} = k_{a1} \qquad [20b]$$

This model is tested by plotting

$$\frac{M_t}{t} \quad \text{against} \quad \frac{1}{t}\ln\left\{\frac{M_\infty}{(M_\infty - M_t)}\right\}$$

which should give a straight line. The slope of the line yields $(M_\infty(1+b)/b)$. The intercept of the line yields $-M_\infty k_{a1}/b$.

Figures (6 and 7) show the resulting plots and table 2 gives the rate constants corresponding to some of the plots shown.

Let us assume that strong adsorption of products occurs. In this case the rate of reaction is

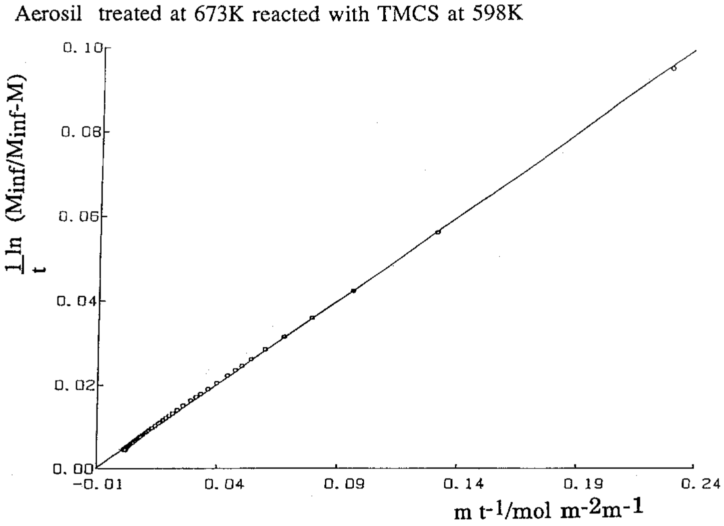

Fig. 6. A plot of the integrated equation for the first order retarded reaction model

Table 2. Rate constants for the chemisorption of TMCS on Aerosil at various temperatures

run number	rate cons.
9	1.0E-6
8	8.4E-6
4	1.6E-5
3	9.7E-5

inversely proportional to the pressure of the products:-

$$\frac{d\theta}{dt} \propto \frac{1}{P'}$$

but from equation (16)

$$P' = K''\theta$$

$$\Rightarrow \frac{d\theta}{dt} = \frac{k_{a1}}{K''\theta}\left\{\frac{1-\theta}{1+b\theta}\right\} \qquad [21a]$$

once again neglecting $b\theta^2$, this integrates to:

$$-\ln(1-\theta) - \theta = k_{a1}t \qquad [21b]$$

where k_r in the present case represents k_a/K''

On substitution as before, equation (21b) yields:

$$k_{a1} = \frac{1}{t}\ln\left\{\frac{M_\infty}{(M_\infty - M_t)}\right\} - \frac{M_t}{tM_\infty} \qquad [22]$$

The model is tested in the same way by a plot of

$$\frac{M_t}{t} \text{ against } \frac{1}{t}\ln\left\{\frac{M_\infty}{(M_\infty - M_t)}\right\}$$

which should be linear. It is possible to distinguish between the two (equations [20b] and [22]) on the basis of intercept.

The effect of temperature on the rate of reaction

Aerosil samples used in this study were all pretreated at 673 K. The silylation temperatures are given in Table 1. The rate constants at four different temperatures obtained from plots according to the integrated equation are given in Table 2. The pretreatment Temperature was 673 K.

Figure 8 is a plot of $\ln k_r$ against $1/T$, according to the Arrhenius equation from the results in the above table ($k_r = A \cdot \exp(-E/RT)$ for TMCS.

When using the Arrhenius equation for the calculation of activation energy, it must be remembered that the equation assumes that the same process occurs at all the temperatures involved. This is not always so; hence in those cases, the energy obtained is not correct. In the present work, no side reactions, other than that of the haloacid, have been observed. It is, therefore, reasonably safe to assume that the same reaction occurs at all the temperatures used.

The energy of activation E (calculated from the gradient, which is equal to E/R) is: 155 kJ mol^{-1}

The value of the energy of activation for the chemisorption of TMCS on Aerosil obtained in this work is identical to the values obtained by other workers [2, 7, 15]. Some of these workers used different experimental and analytical techniques such as infrared spectroscopy [5] and mass

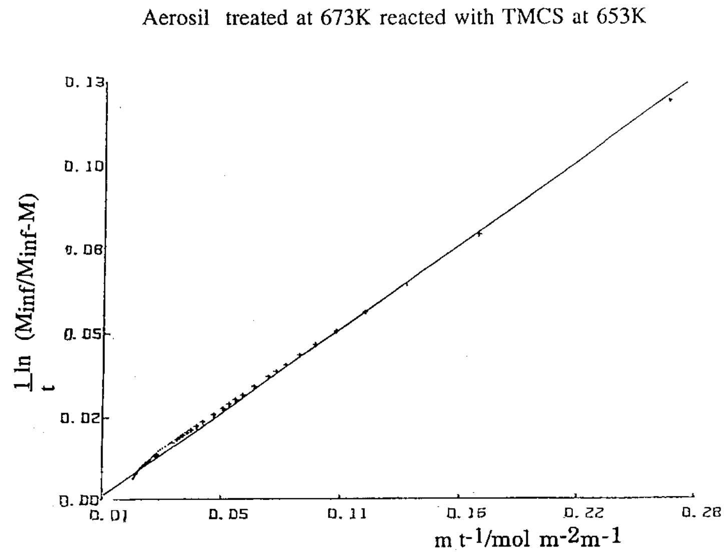

Fig. 7. A second plot of the integrated equation for the first order retarded reaction at a higher temperature (653 K). It shows the poor fitting at the start and at the end of the reaction at this temperature

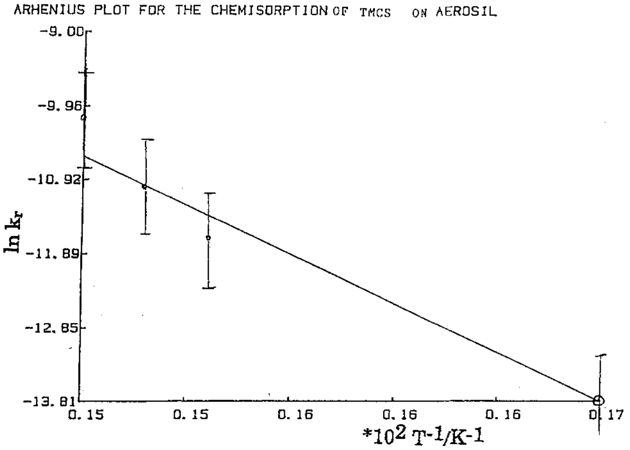

Fig. 8. The plot of $\ln k_r$ against $1/T$, according to the Arrhenius equation

spectroscopy [6], and others used similar experimental techniques but different analytical approaches [15, 6]. Similarity in the energy of activation obtained here to those in the literature presents additional evidence for the validity of the model used in this analysis.

The chemical reaction model results in a multiplicity of rate constants. For silica, these various rate constants, and hence their corresponding activation energies, have been associated with the various types of silanols at the surface [6]. However after evacuation at 673 K only isolated monoenergetic silanols are present at the surface. Therefore, theoretically, only one rate constant should result. However, if addition of the haloacid across the strained siloxane bond occurs, and is much slower than the silylation reaction, the resulting silanols would be consumed at the rate of their production. This would represent the second reaction and would account for only the second rate constant, leaving the third and in some cases the fourth unaccounted for.

The model based on retardation of reaction by one of the products gives only one rate constant for TMCS. This is in accordance with the monoenergetic nature of the isolated silanols remaining on the surface. However, in some cases the plot is still curved at the start of the reaction and more often at the end, especially at the higher temperatures such as 673 K (see Fig. 7) implying that the model probably does not fit the whole range of data.

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