# A STUDY OF THE REACTION OF HEXAMETHYLDISILAZANE WITH SOME COMMON GAS–LIQUID CHROMATOGRAPHIC SOLID SUPPORTS AND ITS EFFECT ON THEIR ADSORPTIVE PROPERTIES

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## INTRODUCTION

Gas–liquid chromatographic peak tailing and retention volume abnormalities, observed primarily at low solvent/support ratios, have generally been attributed to adsorption by uncovered solid support. In addition, although the evidence is somewhat conflicting, there have been several claims[1-5] that isomerisation and decomposition of solutes may also result from the adsorption. These phenomena have been considered sufficiently important to warrant a number of attempts to reduce or to eliminate the adsorptivity of conventional solid supports; a review of the approaches adopted up to now was given in an earlier publication[6], in which the use of hexamethyldisilazane to modify Sil-O-Cel firebrick was described. The success of the silazane treatment has led us to study its application to some of the other siliceous supports which are commonly used and also to investigate more fully the course of the treatment reaction and its consequences. The basis of this study was the direct determination of isotherms for adsorption of vapours by the supports. Acetone and benzene, both of which frequently show gas–liquid chromatographic peak tailing, were chosen for use.

In addition to the adsorption studies, the kinetics of the various solid–silazane reactions were studied at 67° in order to provide information as to the nature and consequences of the treatment.

As previously described[6], preliminary experiments in which conventional volumetric or gravimetric adsorption methods were used gave very unsatisfactory results, and the only approach which proved feasible was the method of frontal chromatography. This technique had only previously been used by JAMES AND PHILLIPS[7] in a study of the adsorption of benzene by a high area active charcoal. Despite the low areas involved in this work the technique gave satisfactory and reproducible results while being technically simple and straightforward in operation.

## APPARATUS

A block diagram is shown in Fig. 1. Oxygen-free cylinder nitrogen passed through a molecular sieve (Linde 4A) silica gel drying train and was then divided into two

streams. The second stream passed successively through the needle valve C, the capillary manometer D and the Foxboro restrictor E, before entering the spiral vapour saturator F, which was suitably thermostatted to within 0.1°. The efficiency of the saturator was carefully checked over a range of gas flow rates which extended
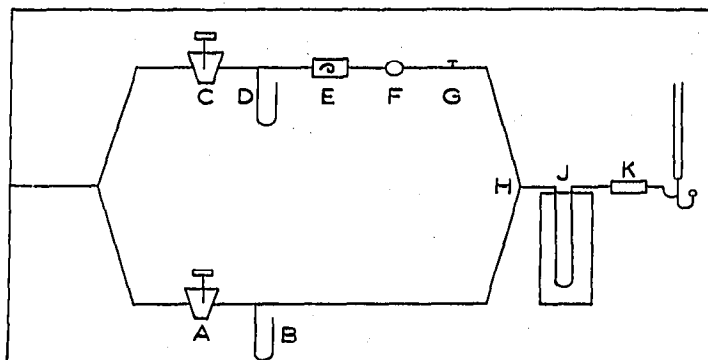


Fig. 1. Block diagram of the apparatus.

well beyond any subsequently used in the adsorption experiments. Under the chosen experimental conditions the saturation vapour pressures of the two substances were about 60 to 70 mm Hg, a value which was a convenient maximum for the experiments.

The two flow streams rejoined at H and then entered the chromatographic column J, which was constructed in 1/4 in. o.d. copper tube. The column was contained in a copper cylinder through which constant temperature water was circulated. The latter was derived from a large bath heated and regulated by a Techne unit which maintained the temperature constant to 0.01°. Circulation was effected by use of a high speed pump. The maximum temperature change during circulation was 0.1°; this degree of control of the column temperature was considered adequate.

On leaving the column the gas stream passed through a single channel, hot wire katharometer, K. This formed one arm of a bridge which was completed with two 50$\Omega$ fixed resistors and a 100$\Omega$ Helipot. Fine control was provided by use of a centre tapped 5$\Omega$ Helipot. The bridge current was derived from an Ediswan low voltage D.C. source which was adjusted to any desired value by means of a series connected 100$\Omega$ Helipot. A bridge current of 70 mA was used throughout the experiments. The use of a single channelled detector was dictated by the need to observe and measure any small flow changes which might occur. For these reasons, too, the katharometer design chosen for use was one giving the maximum flow sensitivity compatible with its use as a thermal conductivity device. The bridge signal was recorded by a Foxboro e.m.f. 1 mV Dynalog recorder.

EXPERIMENTAL PROCEDURE

*Determination of isotherms*

The flow resistance offered by the saturator was negligible and, to all intents and purposes, constant. The restrictor E thus acted as a capillary flow meter for the vapour saturation flow stream and was calibrated with a suitable setting for each of the columns used before commencing the experiments.

In operation, nitrogen was allowed to flow through valve A into the column, valve C being totally closed. A gas–vapour mixture of desired composition was then directed to the column by rapidly partially opening C and simultaneously partially closing A. The total flow was maintained constant by observation of the manometers and the whole operation could be carried out very rapidly. This was followed as soon as possible by injection of a small sample of hydrogen through the septum G. The chromatogram produced consisted of an elution peak of hydrogen followed by a sigmoid step as the vapour broke through.

Knowing the pressures recorded by B and D, the total gas flow at the column outlet, and the saturation vapour pressure of the liquid used at the temperature of the saturator, the concentration of vapour in the mixed gas stream was readily calculated from the calibration data. The vapour steps on the chromatogram were very sharply defined, the tail of the hydrogen peak, on the other hand, was often quite broad. This occurred because it was injected into the slow moving saturator stream and, in addition, the elution technique leads to much greater band broadening than does the frontal method. The latter statement is substantiated by the fact that the four and half feet long columns used in this work yielded up to 12,000 theoretical plates as computed from GLUECKAUF's equation[8]. BOEKE[9] has recently turned this to good account in a method of industrial process analysis where large samples are, of course, readily to hand.

The distance on the chart between the hydrogen peak and the point of inflexion of the vapour step gave the vapour retention (hold-up) time, $t_v$, on the very reasonable assumption that hydrogen is not adsorbed. The total flow rate (nitrogen + vapour) was measured during the experiment so the flow rate of vapour could readily be calculated. The product of this flow rate and $t_v$ gives the volume of vapour adsorbed by the column packing, at the partial pressure of the vapour in the gas stream.

Following the first run, further points on the adsorption isotherm were obtained by stepwise increase of the proportion of the total flow passing through the saturator. With each change of concentration of vapour it was necessary to measure the column outlet flow rate, since it was impossible when adjusting the ratio of the flow from the two streams, to maintain the total rate absolutely constant from run to run. However, the change was usually no more than 1 ml/min out of a total flow rate of about 50 ml/min. The other source of flow rate change, the variation of viscosity due to sorption during a run, was shown to be negligible since the katharometer used would record 1 % full scale deflection per 0.1 ml/min flow change ($\simeq$ 0.2 % of total flow). At no time was a measurable drift or shift of the base line noted. That the measurements were, in any case, unaffected by flow rate was proved by duplication of isotherms at flow rates as far apart as 30 and 60 ml/min.

*Kinetics of treatment*

The rate and course of the treatment reaction were followed by use of a reflux system through which a slow stream of dried nitrogen entrained away any ammonia formed by

$$(CH_3)_3SiNHSi(CH_3)_3 + 2(\cdot OH) = 2[\cdot OSi(CH_3)_3] + NH_3$$

The ammonia passed into a 10 % aqueous boric acid solution and was titrated there with 0.1 $N$ HCl using bromcresol green as indicator[10]. Reasonably close nitrogen flow control was necessary since a small amount of the silazane was carried over and yielded ammonia by hydrolysis in the acid solution. Blank experiments under controlled conditions gave the appropriate correction factors. In each of the experiments a standard weight of 8.33 g of solid was used, this being dispersed in about 50 ml of petroleum ether (60–80°). The solid was rigorously dried before treatment by heating for three days at about 150°.

<div align="center">RESULTS</div>

*Adsorption by untreated supports*

Isotherms for the adsorption of both acetone and benzene at 50° by each of five untreated solids are shown in Fig. 2. Those for pink Chromosorb and Sil-O-Cel firebrick are coincident for acetone but the former is a slightly stronger adsorbent for benzene.
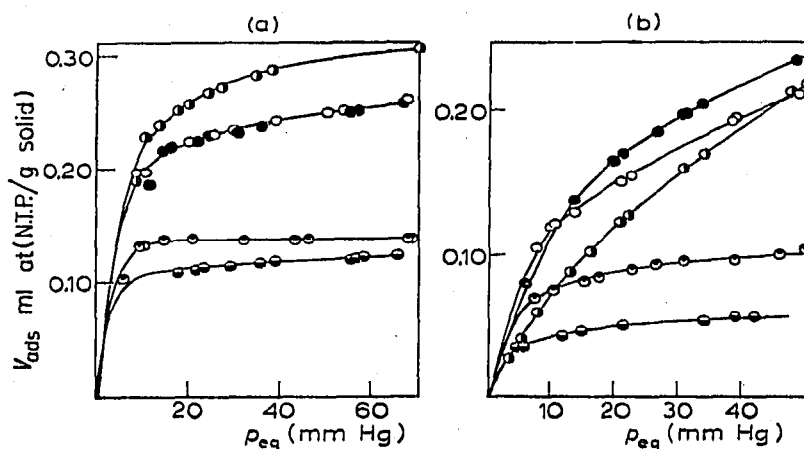


Fig. 2. Isotherms for the adsorption of (a) acetone, (b) benzene at 50° by: O, Sil-O-Cel; ●, Chromosorb (pink); ◑, Chromosorb (pink) acid washed; ◓, Chromosorb-W; ◒, Celite 545.

Acid washing of Chromosorb increases the adsorption of acetone but slightly reduces adsorption of benzene. For these materials, therefore, acid washing before use in gas–liquid chromatography, with its attendant difficulty and expense, is not worthwhile. However, this view cannot be extended to all types of solute simply on the basis of these results.

The isotherms for adsorption by untreated Celite 545 and Chromosorb-W (white) bear the same relation to each other as do those of Sil-O-Cel and pink Chromosorb, the Chromosorb-W being somewhat the stronger adsorbent. On a weight basis, the white solids adsorb only about one-third as strongly as the pink solids. However, they also have much lower bulk densities and so, for a given length of column of fixed diameter, the amount of adsorption by a white support would be only about one-fifth that occurring if a pink support were used. From this point of view, therefore, Celite and Chromosorb-W are considerably better support materials for gas–liquid chromatography. This view is commonly accepted on the basis of chromatographic evidence.

Isotherms for the adsorption of both vapours by Sil-O-Cel and by Celite were determined at three temperatures. Because of the similarities commented on above, and the near identity of physical properties such as density, there is good reason to suppose that Sil-O-Cel and Chromosorb are identical, the same being true of the Celite and Chromosorb-W. Differences in adsorptivity which are observed, therefore, probably represent variations from batch to batch. In consequence, the studies with the Chromosorbs were restricted to 50°. Thus, eighteen isotherms were obtained altogether. Since not all of the isotherms gave linear Langmuir plots the B.E.T. equation, in the form

$$\frac{p_{eq}}{V(p_0 - p_{eq})} = \frac{1}{V_m \cdot C} + \frac{C-1}{V_m \cdot C} \cdot \frac{p_{eq}}{p_0}$$

was applied to the data, and in every case gave an excellent straight line. Fig. 3 illustrates this for adsorption of both vapours by Sil-O-Cel, while Table I summarises the data for all the systems in terms of values of the intercept $(1/V_m \cdot C)$ and the slope $[(C-1)/V_m \cdot C]$.
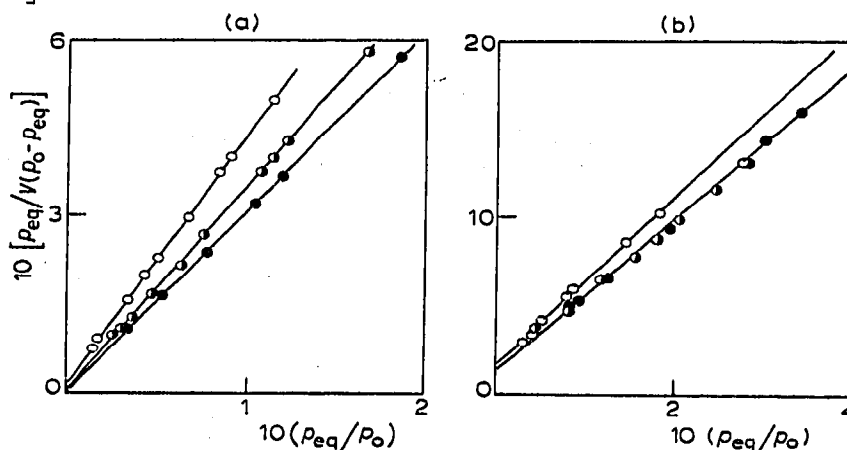


Fig. 3. B.E.T. plots of Sil-O-Cel adsorption data for (a) acetone, (b) benzene.
○, 50°; ◑, 40°; ●, 30°.

The isotherms for the untreated materials are all of Type II which is consistent with the finding that in each case the molar heat of adsorption $(\Delta H^a)$ was greater than the heat of liquefaction $(\Delta H^l)$. Because of the difficulties involved in evaluating isosteric heats from the isotherms, the experimental points being relatively so close to the saturation limit, the net heats $(\Delta H^a - \Delta H^l)$ were, in fact, calculated from values of $C$ derived from the data of Table I. They are, therefore, of no great precision but are adequate to show the sign and magnitude and are listed in Table II.

The data further illustrate the comparable behaviour of Sil-O-Cel and Chromosorb and of Celite and Chromosorb-W already commented on. The values of the net heats for benzene quoted in the table compare with those found by KISELEV[11] in a study of the adsorption of benzene by silica gels of high activity. Quantitative comparison is not possible but KISELEV found, for example, that at low coverage on fairly highly hydroxylated surfaces, monolayer heats were as high as 4900 cal/mole.

Table III lists the surface areas calculated from the volumes of benzene and

## TABLE I

SUMMARISED B.E.T. PLOT DATA FOR UNTREATED SUPPORTS

| Support | Temp. °C. | Acetone | | Benzene | |
|---|---|---|---|---|---|
| | | $\dfrac{C-1}{V_m \cdot C}$ | $\dfrac{1}{V_m \cdot C}$ | $\dfrac{C-1}{V_m \cdot C}$ | $\dfrac{1}{V_m \cdot C}$ |
| Sil-O-Cel | 50 | 4.24 | 0.012 | 4.93 | 0.15 |
| | 40 | 3.42 | 0.004 | 4.10 | 0.15 |
| | 30 | 3.10 | 0.004 | 4.10 | 0.15 |
| Celite | 50 | 9.04 | 0.020 | 20.5 | 0.20 |
| | 40 | 8.83 | 0.005 | 15.6 | 0.03 |
| | 30 | 7.55 | — | 11.5 | — |
| Chromosorb (pink) | 50 | 4.29 | 0.015 | 3.96 | 0.19 |
| Chromosorb (pink) (acid washed) | 50 | 3.37 | 0.025 | 3.30 | 0.43 |
| Chromosorb-W | 50 | 7.75 | 0.005 | 11.9 | 0.11 |

## TABLE II

NET HEATS OF ADSORPTION $(\Delta H^a - \Delta H^l)$ CAL/MOLE
ON UNTREATED SUPPORTS

| Support | Acetone | Benzene |
|---|---|---|
| Sil-O-Cel | 4000 | 2100 |
| Chromosorb | 3700 | 2000 |
| Chromosorb (acid washed) | 3200 | 1400 |
| Celite | 4400 | 3400 |
| Chromosorb-W | 4700 | 3000 |

## TABLE III

SURFACE AREAS FOR UNTREATED SOLIDS CALCULATED
FROM BENZENE AND ACETONE ADSORPTION

| Solid | Temp. °C | Benzene area/g solid $m^2$ | Acetone area/g solid $m^2$ |
|---|---|---|---|
| Sil-O-Cel | 50 | 1.7 | 1.7 |
| | 40 | 2.1 | 2.1 |
| | 30 | 2.1 | 2.4 |
| Celite | 50 | 0.42 | 0.82 |
| | 40 | 0.56 | 0.84 |
| | 30 | 0.76 | 0.98 |
| Chromosorb (pink) | 50 | 2.2 | 1.7 |
| Chromosorb (pink) (acid washed) | 50 | 2.4 | 2.1 |
| Chromosorb-W | 50 | 0.73 | 0.96 |

acetone adsorbed in the monolayer $(V_m)$ on the assumption[12,13] that the benzene molecular cross-sectional area in adsorption by silica is 32 Å$^2$, and from a comparison of the data for Sil-O-Cel, that the acetone area is 26.5 Å$^2$.

The areas computed for the pink solids (Sil-O-Cel, Chromosorb) agree as closely as may be expected in the light of the probable errors of measurement and those inherent in the B.E.T. method. On the other hand, those derived from the benzene data for Celite show internal inconsistency which is sufficiently great to suggest that the data are unreliable for area determination. Further point is given to this by the finding that while the ratio $(V_m)_{acetone}/(V_m)_{benzene} = 1.2 \pm 0.2$ for all the pink solids, this ratio varies from 1.5 to 2.2 for the white solids. The variation of $(V_m)_{acetone}$ for Celite adsorption is small compared to that of $(V_m)_{benzene}$. This again suggests that the data for acetone are the more reliable. On this basis we take the mean area of the pink solids to be 2.1 m$^2$/g.

### Adsorption by treated supports

Isotherms for the adsorption of both acetone and benzene by treated Sil-O-Cel and Celite 545 are shown in Figs. 4 and 5 respectively. The data for all the systems studied yielded reasonably straight lines when plotted according to the B.E.T. equation. Fig. 6 illustrates such plots for the adsorption of acetone by treated firebrick over the temperature range 30–50° while Fig. 7 shows similar data for adsorption of benzene by Celite 545. These represent the best and worst fit, respectively. For brevity, the detailed surface area measurements are not included, the mean values derived being 0.6 m$^2$/g for the pink solids and 0.25 m$^2$/g for the white supports. No attempt was made at evaluation of net heats of adsorption due to the smallness of $V_m$ in each case



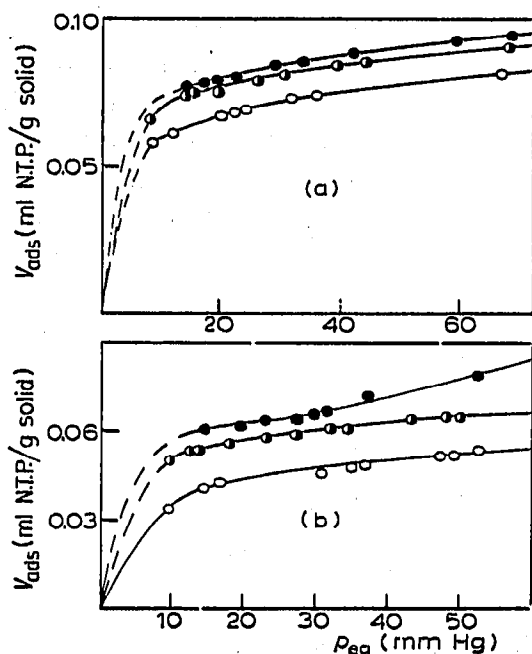Fig. 4. Isotherms for the adsorption of (a) acetone, (b) benzene by hexamethyldisilazane treated Sil-O-Cel. O, 50°; ◑, 40°; ●, 30°.
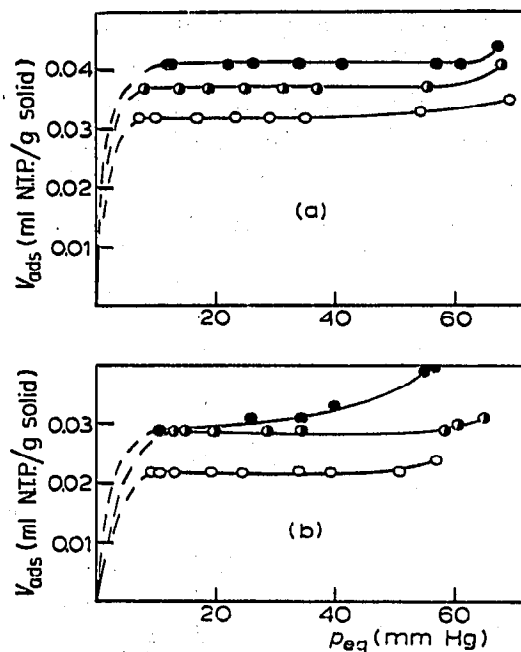
Fig. 5. Isotherms for the adsorption of (a) acetone, (b) benzene by hexamethyldisilazane treated Celite 545. O, 50°; ◑, 40°; ●, 30°.
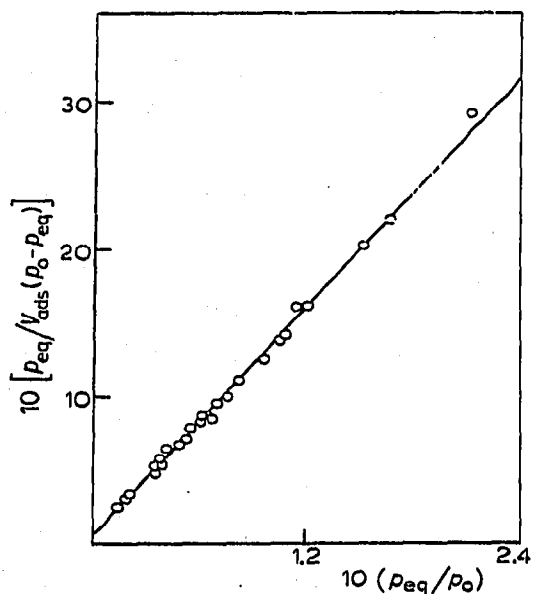
Fig. 6. B.E.T. plots of adsorption of acetone by hexamethyldisilazane treated Sil-O-Cel at 30°, 40° and 50°. Points are not distinguished since they lie close to a common line.
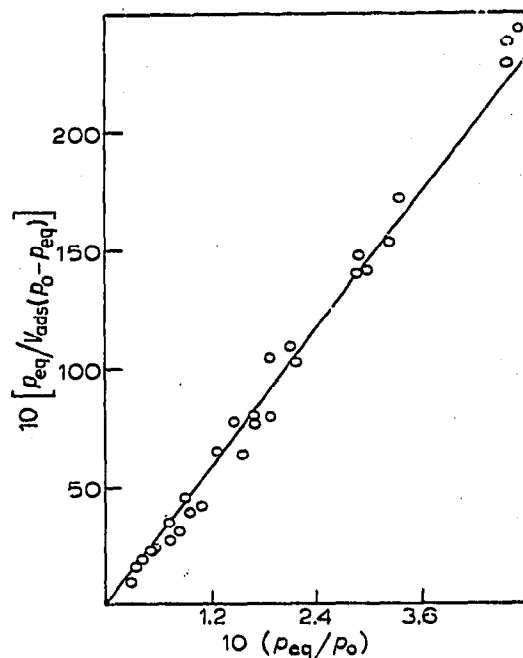
Fig. 7. B.E.T. plots of adsorption of benzene by hexamethyldisilazane treated Celite 545 at 30°, 40° and 50°. Points are not distinguished since they lie close to a common line.

but rough estimation indicated that they differed little from those for the untreated materials.

*Kinetics of treatment*

The rate of ammonia evolution per gram of Sil-O-Cel firebrick at 67° was measured at three disilazane/firebrick ratios which corresponded to the use of 5 ml, 2 ml, and 1 ml of disilazane with 8.33 g of brick. The total ammonia evolved at "infinite" time ( ~ 20 h) was experimentally determined in each case and the results indicate that the reaction is quantitative since, for both the reactions involving 2 ml and 5 ml of disilazane, it was found to be $6.6 \cdot 10^{-5}$ moles/g of brick. For convenience in presen-
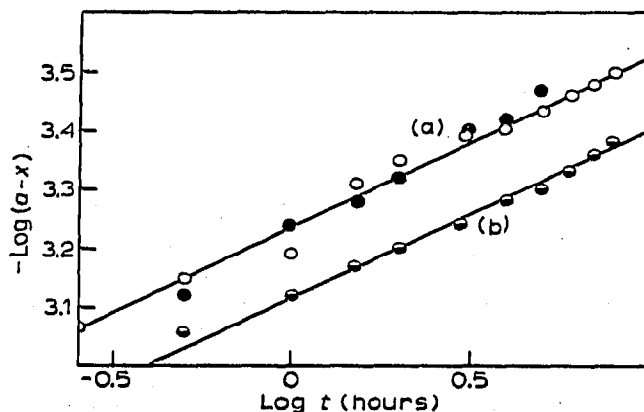


Fig. 8. Order of reaction plots for (a) Sil-O-Cel, O, 2 ml and ●, 5 ml hexamethyldisilazane; (b) Chromosorb (pink), 5 ml hexamethyldisilazane.

tation the kinetic data are presented in the form of log $(a - x)$ *versus* log $t$ plots, $a$ being computed from the infinite time result. The linearity of this unconventional plot permits approximate evaluation of order w.r.t. solid as about 4. A first order plot appeared as two intersecting straight lines, the initial rate being comparable with that for Celite (see below), the later rate being much smaller. This may indicate concurrent reaction of high and low activity groups or inhibition through restricted availability. Either would suggest the apparent high overall order.
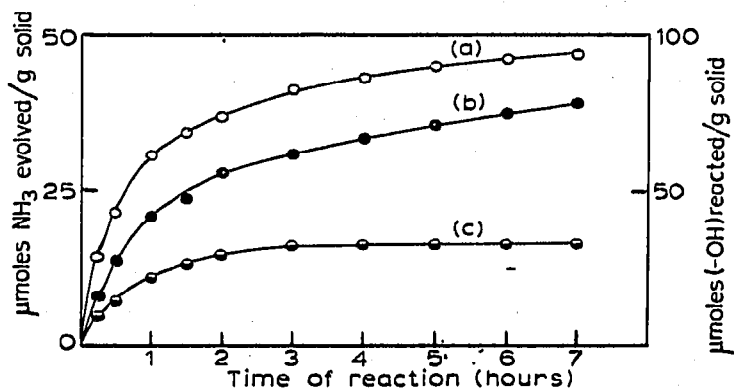
Fig. 9. Ammonia evolution as a function of the time of reaction with hexamethyldisilazane at 67° of (a) Sil-O-Cel, (b) Chromosorb (pink) and (c) Celite 545.

Fig. 9 shows a comparison of the rates of ammonia evolution from equal weights of Sil-O-Cel firebrick, Chromosorb (pink) and Celite 545. A log/log plot of the rate data for pink Chromosorb is also shown in Fig. 8 and again the order with respect to the solid appears to be 4.3, as was found for Sil-O-Cel. Celite 545, however, gave a curved log/log plot and it was found that, as shown in Fig. 10, the data obeyed a
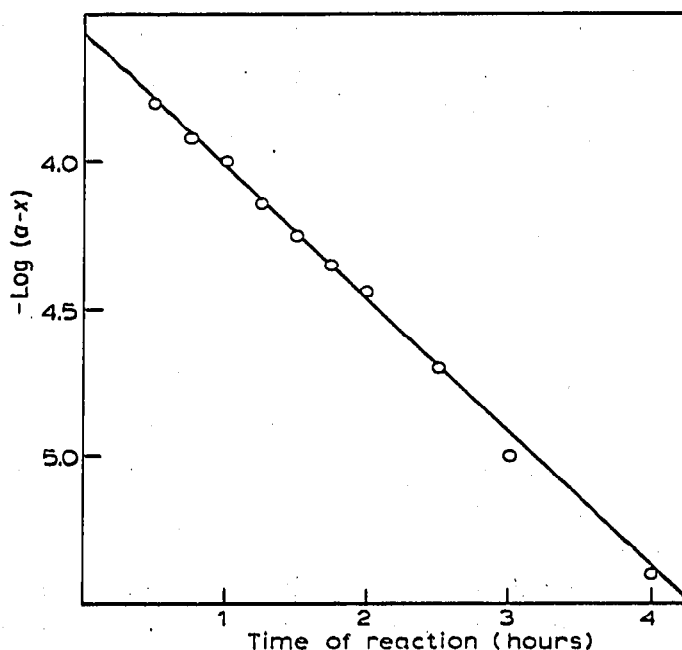
Fig. 10. First order rate data plot for the reaction of Celite 545 with hexamethyldisilazane at 67°.

first order equation. The difference in order observed is perhaps accounted for by the structural differences between the pink and the white solids which can be demonstrated to exist by the considerable difference in their densities and liquid absorption characteristics.

The infinite time values for ammonia evolution yield the result that for Sil-O-Cel the surface concentration of hydroxyls is $4 \cdot 10^{19}$ groups/m$^2$ while for Celite it is about $2.5 \cdot 10^{19}$ groups/m$^2$. These values correspond to an apparent hydroxyl group area of 2.6 Å$^2$ for Sil-O-Cel and 4.5 Å$^2$ for Celite. This implies that there is very complete hydration of the surfaces since the (Si-O) bond length in silica[14] is about 1.6 Å. Again, it may be concluded that the reaction is quantitative since the surface cannot reasonably accommodate in a monolayer many more hydroxyl groups or water molecules than is indicated by the results.

It was suggested elsewhere[6] that the addition of $n$-propanol facilitated the treatment but this is now known to be true only at very high silazane concentrations. Equally good results can be obtained, with great economy of reagent, by use of a 6 % silazane petroleum ether solution without additive. The ratio of solution to solid should be not less than four. The time of treatment can be deduced from Fig. 9. At higher temperatures, of course, reaction is likely to be more rapid but loss of silazane may become appreciable.

## DISCUSSION

The surface area determined in this work for Celite accords with previous measurements[15-17]. That for the pink solids, however, is about half the value found by BAKER et al.[16] and about two-thirds of that found by NELSEN AND EGGERTSEN[17], both using low temperature nitrogen adsorption. The discrepancies in these measurements are not readily explained, but it seems reasonable to accept that the areas appropriate in considering adsorption by uncovered support in gas–liquid chromatography are likely to be those determined for vapours in chromatographic conditions. In our earlier work[6] an area of 3 m$^2$/g was derived for Sil-O-Cel, the difference between this and the value quoted here arising entirely through the use of Langmuir plots in the previous publication. The more general linearity of B.E.T. plots observed in this, the wider study, justifies their use rather than those based on the Langmuir equation and the consequent preference for the areas calculated here. Further evidence on this point comes from the fact that at the same value of $p/p_0$ the ratio of the amount of benzene adsorbed by Sil-O-Cel to that adsorbed by a highly active silica gel[13] is almost identical with the ratio of the surface areas per gram. This result, in turn, suggests most strongly that the siliceous supports act merely as low area silica gels in adsorption and that the only differences in adsorptivity between the treated and untreated supports results from area differences.

It is clear from the results that treatment with hexamethyldisilazane is beneficial for all the supports studied. Thus, for example, from the point of view of adsorption, treated Sil-O-Cel compares closely with untreated Celite, while the least adsorptive

material is a treated white solid. It may be pointed out here that adsorption isotherms determined for a sample of Chromosorb-W treated with dimethyldichlorosilane (kindly supplied by Johns Manville Ltd.) showed it to be about twice as strong an adsorbent as silazane treated material.

One consequence of the silazane treatment is clearly a reduction of available adsorptive surface area. For each solid the area ratio of treated/untreated material is 0.28 and it is a point of interest that the saturation values of the amount of benzene or acetone vapour adsorbed by treated and untreated solid are in exactly the same ratio. Thus, the treatment may be more effective either through production of a completely inert surface where reaction has occurred, or by blocking up the pores and rendering the internal surface of the particles unavailable. If the latter is the case, it is possible that the treatment might adversely affect the ability of the support to carry solvent. As a check on this, the abilities of the treated and untreated solids to take up an involatile solvent was studied. It was found that they were identical in their capacity, the first signs of dampness appearing for both at 70 % w/w, polyethylene glycol/Sil-O-Cel. Since the polyglycol molecules are considerably bigger than those of either benzene or acetone this result might be taken to favour the view that the consequence of the treatment is the formation of a relatively inert surface.

## ACKNOWLEDGEMENTS

## SUMMARY

The reaction of hexamethyldisilazane with five common gas–liquid chromatographic solid supports has been studied. Kinetic data have been obtained for the reactions with Sil-O-Cel and Celite. Isotherms for the adsorption of acetone and benzene vapours (30–50°) by treated and untreated samples of all the solids have been determined. The results show that adsorption by the solid support is reduced very significantly after treatment, the reduction being brought about predominantly by a change in the available surface area. This change is thought to result from loss of active sites and not from blocking of pores with the consequent loss of internal area. The least adsorptive support found is silazane treated Celite (or Chromosorb-W); at 50° the amount of acetone vapour adsorbed at the saturation limit is only 1.4 $\mu$moles/g.

## REFERENCES

1 G. A. P. TUEY, in D. H. DESTY, *Gas Chromatography 1958*, Butterworths, London, 1959, p. 215.
2 A. LIBERTI, *ibid.*, p. 214.
3 A. Z. CONNER, *ibid.*, p. 214.
4 J. JANÁK, *ibid.*, p. 329.
5 T. JOHNS, in V. J. COATES, H. J. NOEBELS AND I. S. FAGERSON, *Gas Chromatography*, Academic Press, New York, 1958, p. 31.

[6] J. BOHEMEN, S. H. LANGER, R. H. PERRETT AND J. H. PURNELL, *J. Chem. Soc.*, (1960) 2444.
[7] D. H. JAMES AND C. S. G. PHILLIPS, *J. Chem. Soc.*, (1954) 1066.
[8] E. GLUECKAUF, *Trans. Faraday Soc.*, 51 (1955) 34.
[9] J. BOEKE, in R. P. SCOTT, *Gas Chromatography 1960*, Butterworths, London, 1960, p. 88.
[10] E. C. WAGNER, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 771.
[11] A. V. KISELEV, in D. H. EVERETT AND F. S. STONE, *The Structure and Properties of Porous Materials*, Butterworths, London, 1958, p. 195.
[12] H. K. LIVINGSTON, *J. Colloid Sci.*, 4 (1949) 450.
[13] D. W. McKEE, *J. Phys. Chem.*, 63 (1959) 1256.
[14] R. B. SOSMAN, *The Properties of Silica*, The Chemical Catalog Company, Inc., New York, 1927, p. 234.
[15] S. DAL NOGARE, private communication.
[16] W. J. BAKER, E. H. LEE AND R. F. WALL, *2nd Intern. Symp. of Instrument Society of America*, Lansing, Mich., June 1959.
[17] F. M. NELSEN AND F. T. EGGERTSEN, *Anal. Chem.*, 30 (1958) 1387.