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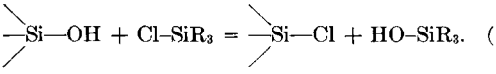
LETTERS TO THE EDITORS

Comment on: "Adsorption and Reaction of Methylchlorosilanes at an Aerosil Surface," by B. Evans and T. E. White

A study of the "Adsorption and Reaction of Methylchlorosilanes at an Aerosil Surface" has been published recently by Evans and White (*1*). A similar kinetic study has been carried out in our laboratory and published elsewhere (*2*). The methods of analyzing the data were quite different (Evans and White used gravimetric techniques, whereas we have used infrared spectroscopic techniques) but the choice of experiments and the experimental conditions were quite similar. It is, therefore, of interest to compare the experimental results and conclusions reached from these investigations. Evans and White concluded that: (i) At 30°C, the adsorption of methylchlorosilanes onto surface hydroxyl sites is physical and completely reversible (ii) Above 250°C, the OH groups react chemically with the chlorosilanes. (iii) Reaction rates at any temperature are in the order: $RSiCl_3 > R_2SiCl_2 > R_3SiCl$. (iv) The activation energies are: $R_3SiCl = 37$, $R_2SiCl_2 = 31$, and $RSiCl_3 = 30$, in kcal/mole. (v) The amount of silane uptake is consistent with a mechanism which results in 31–39% of the OH groups reacting on a 2:1 basis.

Our results are in agreement with conclusions (i), (ii), (iii), and (v). Silicon tetrachloride can be added to the reaction rate series (conclusion iii) giving the fastest reaction rate. The experimental activation energies calculated from our results, however, were about 22 kcal/mole for all four chlorosilanes, and are considerably lower than those reported by Evans and White.

We believe this one discrepancy can be clarified. In our experiments the reaction curves were obtained spectroscopically (i.e., by following the decrease in surface OH concentration with time). This data was then plotted using various order integrated rate equations, until a linear plot was obtained. This method has been described in detail elsewhere (*2, 3*). The order of the reaction with respect to the disappearance of hydroxyl groups was then interpreted as the number of OH groups *on average* which are consumed when one chlorosilane molecule reacts with the surface. We found that the monochlorotrimethylsilane reaction gave a 1.0-order kinetic plot (1 OH removed per silane molecule), and that the di-, tri-, and tetrachlorosilanes all gave 1.5 ± 0.2-order kinetic plots (1.5 OH groups removed on average per silane molecule). The 1.5 groups *on average* which are removed per silane molecule correspond to 50% of the OH groups reacting on a 1:1 basis, and 50% on a 2:1 basis. In all our plots a positive intercept was obtained which corresponded to an initial fast reaction of about 10–15% which we ascribed (*2*) in part as due to a direct replacement of the hydroxyl group by a Cl group, via



$$\equiv Si-OH + Cl-SiR_3 = \equiv Si-Cl + HO-SiR_3. \quad (1)$$

That a reaction of this type takes place was shown by the presence of residual

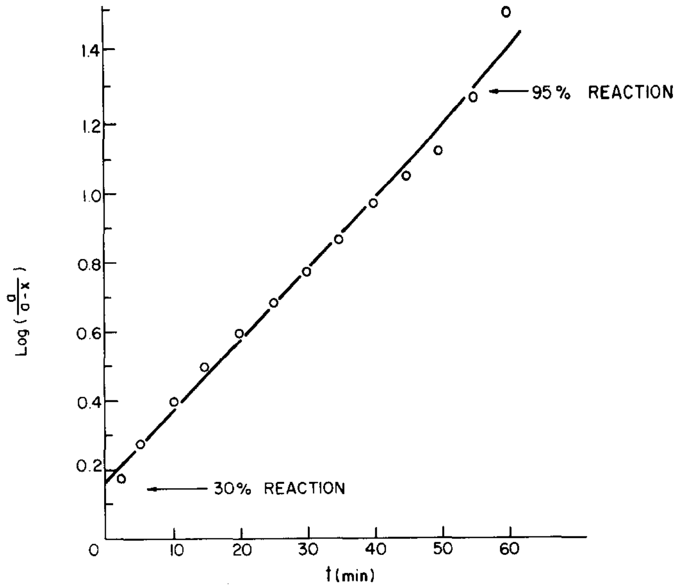


FIG. 1. The 1.0-order kinetic plot for the reaction of monochlorotrimethylsilane with silica; data taken from Fig. 2 of Ref. (*1*).

chlorine on silica samples which had been reacted with monochlorotrimethylsilane.

The reaction curves presented by Evans and White give remarkably good straight lines when plotted using a 1.0-order kinetic plot for the monochlorosilane (Fig. 1) and a 1.6-order kinetic plot for the dichloro- and trichlorosilanes (Fig. 2). With the monochlorosilanes, one would, of course, expect to obtain 1.0-order kinetics if all the surface OH groups are mono-energetic and react randomly. This point, as well as the other assumptions, have been discussed elsewhere (*2*, *3*). In Figs. 1 and 2 it should be noted particularly that a positive intercept is observed which corresponds to about 30% of the total reaction.

The 1.6-order reaction, obtained from

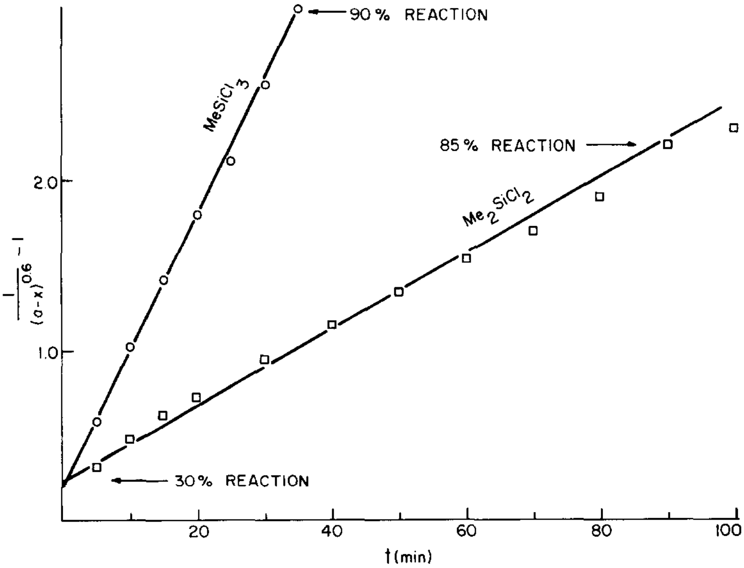


FIG. 2. The 1.6-order kinetic plots for the reactions of trichloromethyl- and dichlorodimethylsilanes with silica; data taken from Fig. 3 of Ref. (*1*).

the kinetic plots in Fig. 2, corresponds to 60% of the chlorosilane molecules reacting with two OH groups and 40% reacting with one OH group (exclusive of the 30% initial fast reaction). If the initial fast reaction takes place on a 1:1 basis, the overall stoichiometry is: (0.7) (1.6) + (0.3) (1.0) = 1.42, or 42% of the OH groups react 2:1 with the chlorosilane, in reasonable agreement with Evans and White's value of 31–39% which they calculated from the relative uptakes of physically and chemically adsorbed silanes. A 1.5-order kinetic function results in an almost linear plot and gives an overall stoichiometry of 35% of the OH groups reacting 2:1, which is in perfect agreement with their calculated values.

The calculations show that a kinetic evaluation of the reaction curves gives the same results as obtained by Evans and White when comparing the uptake of physically and chemically adsorbed silane. The only significant difference noted between the two studies, then, is in the values of the experimental activation energies. In our work these energies were calculated from the values of the rate constants obtained from the kinetic plots, *after the initial fast reaction has taken place,* whereas Evans and White used the half-time of reaction to determine the activation energy. Use of these half-times, however, results only in an overall value which represents the temperature dependence of the sum of the two reactions, and includes contributions from the activation energies of both the initial fast reaction and the slower coupling reaction. Unfortunately, there is insufficient published data available to recalculate the true activation energies.

REFERENCES

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A Comment on Ward and Hansford's Paper "Active Sites on Zeolites IX"

The paper by Ward and Hansford (*1*) (WH) on the infrared bands in NaHY zeolites published recently in this journal contains some very interesting data. We feel, however, that there is an alternative and perhaps more substantial interpretation of this data than the one presented by the authors. In view of the fact that WH refers to the X-ray data of Eulenberger, Shoemaker, and Keil (*2*) (ESK) on sodium Y zeolite, and to our recent assignment of proton positions in HY (*3*), it is surprising that the authors of WH do not consider this explanation.

Despite the experimental work of ESK* giving the Na^+ distribution in NaY, the authors of WH rely heavily on the rather idealized site occupancies given by Breck

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*The data of ESK brings out the important point (see also Dempsey (*5*)) that perhaps the elusive site III cations (referred to by Breck (*4*) are more correctly site I′ cations; i.e., the energetics of the situation for monovalent cations in Y faujasites may be such that site I′ is always occupied in preference to the hypothetical site III on the square faces of the sodalite cage—even at the expense of occupying a site I and a site I′ simultaneously.