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# CLAY-CATALYZED REACTIONS IN ORGANOSILICON CHEMISTRY THE INTERCHANGE OF HYDROGEN AND SILOXY LIGANDS ON SILICON

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Acidic clays are effective catalysts for the redistribution and polymerization of organosiloxanes[1-3]. The similarity of these reactions to conventional acid-catalyzed polymerizations[4] suggests that the activity of the clays might be due to adsorbed mineral acid[1]. However, other investigations have shown that the activity of acidic clays is commonly due to either Lewis or Brönsted acid sites on the clay surface itself. (For a discussion on the catalytic activity of acid clays see ref. 5.)

During our attempts to elucidate the mechanisms of reactions catalyzed by clays and by silica–alumina, it was found that many acidic clays catalyze the interchange of hydride and siloxy groups on silicon. For example, dimethylsilane was produced in 85% yield when sym-tetramethyldisiloxane was heated to 60–110° with clays such as kaolinite, halloysite, montmorillonite and some synthetic mordenites in the hydrogen form. When pentamethyldisiloxane was heated with the above clays, approximately 80% of the SiH was collected as trimethylsilane and dimethylsilane in a mole ratio of 1 to 3.

$$(\mathrm{Me_2HSi})_2\mathrm{O} \xrightarrow[60-100^\circ]{\text{Clay}} \mathrm{Me_2SiH_2} + \mathrm{Me_2HSiO(Me_2SiO)}_x\mathrm{SiMe_2H} \qquad (1)$$

$$\begin{aligned}\mathrm{Me_3SiOSiMe_2H} \xrightarrow[110^\circ]{\text{Clay}} &\ \mathrm{Me_3SiH} + \mathrm{Me_2SiH_2} + \mathrm{Me_3SiO(Me_2SiO)}_x\mathrm{SiMe_3}\\ &+ \mathrm{Me_2HSiO(Me_2SiO)}_x\mathrm{SiMe_3} + \mathrm{Me_2HSiO(Me_2SiO)}_x\mathrm{SiHMe_2} \qquad (2)\end{aligned}$$

When dimethylsilane was allowed to evolve from the reaction in eqn. (1), an average degree of polymerization, $\bar{x}=129$ was obtained and other siloxanes with $x=0$ through 7 could be isolated. The compounds, 1,3-dimethyl-1,3-diethyldisiloxane and 1,1,3,3-tetramethyl-1-propyldisiloxane showed the same types of reactions as illustrated in eqns. (1) and (2). The only effect of increased organic content was to decrease the reaction rate.

Similar product distribution as shown in eqn. (2) were obtained when equivalent quantities of dimethylsilane and hexamethyldisiloxane were reacted under identical conditions. This reaction indicates that the exchange is intermolecular. The results of this investigation are summarized in Table 1.

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TABLE 1

SILOXANES INVESTIGATED FOR HYDROGEN–SILOXY EXCHANGE USING MONTMORILLONITE $H^+$ AS THE CATALYST

| *Starting materials* | *Reaction time (h)* | *Temp.* | *Method*[a] | *Products*[b] *and yields*[c] $R=(Me_2HSi)$, $R'=(Me_3Si)$ |
|---|---|---|---|---|
| $(Me_2HSi)_2O$ | 18 | 60–80° | A.P. | $Me_2SiH_2$ (85% SiH); $RO(Me_2SiO)_xR$ (15% SiH, $\bar{x}=129$) |
| $(Me_2HSi)_2O$ | 24 | 110° | S.T. | $Me_2SiH_2$ (77% SiH); $RO(Me_2SiO)_xR$ (23% SiH) |
| $(MeEtHSi)_2O$ | 24 | 90–110° | A.P. | $MeEtSiH_2$ (68% SiH): $HMe(Et)SiO(MeEtSiO)_xSiMe(Et)H$ (32% SiH) |
| $[Me(Ph)HSi]_2O$[d] | 20 | 80–100° | A.P. | $MeSiH_3$ (80% SiH); Gel |
| $Me_2HSiOSiMe_3$ | 24 | 110° | S.T. | $R'H$ (13% SiH); $Me_2SiH_2$ (67% SiH); $(R')RO(Me_2SiO)_xR(R')$ (20% SiH) |
| $Me_2HSiOSi(Me)_2Pr$ | 24 | 100° | S.T. | $PrMe_2SiH$ (10% SiH); $Me_2SiH_2$ (57% SiH); $RO(Me_2SiO)_xR$ (33% SiH) |
| $Me_2Si(OSiMe_2H)_2$ | 24 | 110° | S.T. | $Me_2SiH_2$ (82% SiH): $RO(Me_2SiO)_xR$ (18% SiH) |
| $MeSi(OSiMe_2H)_3$ | 24 | 110° | S.T. | $MeSi(OR)_3$ (100% SiH) |
| $Si(OSiMe_2H)_4$ | 24 | 110° | S.T. | $Si(OR)_4$ (100% SiH) |
| $(Me_3SiO)_2Si(Me)H$ | 24 | 110° | S.T. | $(R'O)_2Si(Me)H$ (100% SiH) |
| $R'O(MeHSiO)_{30}R'$ | 4 | 173° | A.P. | $H_2$; $R'O(MeHSiO)_xR'$ (>90% SiH) |
| 1.0 $Me_2SiH_2$; 1.0 $R'_2O$ | 24 | 110° | S.T. | $R'H$; $(R)R'O(Me_2SiO)_xR(R')$; RH |
| 4.0 $Me_2SiH_2$; $(Me_2SiO)_4$ | 24 | 110° | S.T. | $RO(Me_2SiO)_xR$, $x=0$–7 (35 wt.%), $x>7$ (59 wt.%); $(Me_2SiO)_4$ (6 wt.%) |
| excess $Me_2SiH_2$; $RO(Me_2SiO)_xR$ $\bar{x}=129$ | 26 | 110° | S.T. | $RO(Me_2SiO)_xR$, $\bar{x}=15$; $x=0$–7 (24 wt. %), (76 wt. %) |

[a] Atmospheric pressure (A.P.) or sealed tube (S.T.). [b] Polymers where $\bar{x}=0$ through 7 were detected by GLC in all cases cited. $\bar{x}$ was determined by the % SiH in the polymer. $\bar{x}>7$ generally made up more than 50% of the polymer formed. [c] Yields are expressed as percent SiH from the starting material (% SiH) or as weight percent (wt.%). [d] Products indicate that Ph–H and/or Ph–OSi≡ exchange occurred.

$$Me_2SiH_2+(Me_3Si)_2O \xrightarrow[110°]{Clay} Me_3SiH+Me_2HSiO(Me_2SiO)_xSiMe_2H \qquad (3)$$

When 1,3-dimethyl-1,3-diphenyldisiloxane was heated with montmorillonite $H^+$, methylsilane and a gel were formed. This observation indicates that in this reaction phenyl–hydrogen and/or phenyl–siloxy exchange occurred in addition to siloxy–hydrogen exchange, extending the possible scope of clay catalyzed redistribution reactions.

$$[Me(Ph)HSi]_2O \xrightarrow[100°]{Clay} MeSiH_3+polymer \qquad (4)$$

Dimethylsiloxy end-blocked polydimethylsiloxanes were obtained from octamethylcyclotetrasiloxane and dimethylsilane in the presence of acidic clays. A dimethylsiloxy end-blocked polydimethylsiloxane polymer with an average degree of polymerization $\bar{x}=129$ was equilibrated to $\bar{x}=15$ when treated with dimethylsilane and acidic clays. These examples illustrate the reversibility of this ligand exchange.

$$4.0\ Me_2SiH_2 + (Me_2SiO)_4 \underset{100°}{\overset{Clay}{\rightleftharpoons}} Me_2HSiO(Me_2SiO)_xSiMe_2H \qquad (5)$$

$$Me_2SiH_2(excess) + Me_2HSiO(Me_2SiO)_{129}SiMe_2H \underset{100°}{\overset{Clay}{\rightleftharpoons}} Me_2HSiO(Me_2SiO)_{15}SiMe_2H \qquad (6)$$

The rate of hydride–siloxy interchange is quite dependent on silane structure. For example, 1,1,1,3,5,5,5-heptamethyltrisiloxane would not rearrange to form methylsilane when heated to 110° in the presence of an acid clay. Compounds with the general formula $(Me_2HSiO)_xSiMe_{4-x}$, where $x = 1$ and 2, would rearrange when treated with acid clays, while compounds with $x = 3$ and 4 did not undergo rearrangement. Generally, the more electron-withdrawing ligands on the parent silicon atom, the less tendency for reaction. This trend in reactivity was opposite from that observed by Zichy[6] and Lee[7] for the reaction of various siloxanes with bases.

$$Me_3SiO\text{–}Si(H)Me\text{–}OSiMe_3 \underset{110°}{\overset{Clay}{\rightleftharpoons}} \text{No reaction} \qquad (7)$$

The acidic clays are unique acid catalyst for this ligand exchange. The more common Lewis or Brönsted acids such as $H_2SO_4$, $AlCl_3$, $BF_3 \cdot Et_2O$, $HCl_{aq}$, $H_2PtCl_6$, $Ti(O\text{-}iso\text{-}C_3H_7)_4$, carbon blacks, etc. did not function as catalysts for the siloxy–hydrogen exchange reaction under similar experimental conditions. In some cases decomposition of the siloxane occurred, but in no case was any dimethylsilane detected.

The catalytic activity of the clays appears to arise from the strong "active sites" on the clay surface. The degree of activity in the clays was found to be somewhat dependent on their structure and the method of activation. Table 2 summarizes the

TABLE 2

CLAY MINERALS AND SYNTHETIC SILICA–ALUMINA AS CATALYST FOR HYDROGEN–SILOXY EXCHANGE IN 1,1,3,3-TETRAMETHYLDISILOXANE

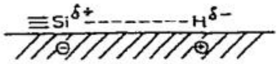
$$(Me_2HSi)_2O \xrightarrow[110°,\ 24\ h]{Catalyst} Me_2SiH_2 + Me_2HSiO(Me_2SiO)_xSiMe_2H$$

| *Clay Minerals* | *GLC area % $Me_2SiH_2$*[a] | *Synthetic Silica–Alumina (Structure)* | *GLC area % $Me_2SiH_2$*[a] |
|---|---|---|---|
| Montmorillonite $H^+$[b] | 77.4 | Zeolon® $H^+$[d] (Mordinite) | 79.5 |
| Kaolinite $H^+$ | 66.4 | Zeolon® $Na^+$ | 0.0 |
| Montmorillonite (Raw)[c] | 68.4 | Houdry® S-46[e] (Amorphous) | 52.0 |
| Halloysite (Raw) | 87.6 | Houdry® S-90 | 0.0 |
| | | Linde® 5A[f] (Zeolite) | 0.3 |
| | | Linde® 13X | 1.2 |

[a] These values represent the percent of the total volatiles eluted from the gas chromatograph at 300°. The remaining volatiles were $x=0$ through 7. Internal standards indicate that 50 to 100% of the injected sample was eluted. [b] Hydrogen-form clays were washed with sulfuric acid and calcined. [c] Raw clays were used as obtained (usually in the $Ca^{2+}$ form) after being heated to 150° for 2 h. [d] Norton Company, Worcester, Massachusetts. [e] Houdry Process and Chemical Company, Philadelphia, Penn. [f] Linde Company, Tonawanda, N.Y.

reactivity of various catalysts evaluated by reaction with sym-tetramethyldisiloxane. Amorphous, synthetic silica–alumina catalyst with small pore size (< 5 Å) and/or a low silica to alumina ratio did not exhibit catalytic activity; nor did silica–alumina in the sodium form. Natural clays in the calcium form and acid washed natural clays were generally active catalysts.

Though ligand exchange was not realized with conventional acids, the current study suggests that it must be classified as an acid-catalyzed reaction. The decreasing reactivity of the siloxane with increasing oxygen substitution on the parent silicon suggests an electrophilic attack near the silicon atom. Attack on the hydride ligand by electron-deficient sites in the clay or a weakening of the silicon hydride bond via chemosorption on strong electrostatic dipoles which were reported to be present in silica–alumina[8], might have occurred to facilitate the interchange of ligands.



This newly discovered reaction may explain the loss of hydride ligand observed by Sakiyama and Okawara[3] when they heated sym-tetramethyldisiloxane and octamethylcyclotetrasiloxane with active clays.

The ligand distribution in every example (see Table 1) indicated a tendency for an accumulation of one ligand on the silicon. This suggests an analogy with the work of Weyenberg and coworkers[9] who noted similar tendencies when studying the redistribution of hydrogen and methoxy groups on silicon. The driving force for the accumulation of oxygen on silicon was attributed to increased bond energy via greater $\pi$ interaction of the ligands with silicon. A recent nuclear magnetic resonance study on alkylalkoxysilanes supports this reasoning[10]. Extensive redistribution studies have recently shown similar tendencies for an accumulation of second row ligands on silicon[11].

This exchange reaction illustrates the unique nature of the catalytic activity of clays and silica–alumina, and may aid in establishing the nature of the "active sites" on these materials.

## EXPERIMENTAL

The various siloxanes used in our investigation were prepared by the hydrolysis of appropriate alkoxy- or chlorosilanes[12].

### *General method for reactions at atmospheric pressure*

sym-Tetramethyldisiloxane (134.2 g, 1.0 mole) was mixed with a sulfuric-acid-washed montmorillonite-clay, Filtrol-13® (2.68 g, 2% by weight) which was used as obtained after being dried at 150° for 2 h prior to use (Filtrol Corporation, Los Angeles, California). This mixture was heated with rapid stirring under a nitrogen blanket. At 73° vigorous boiling occurred, accompanied by a rapid drop in temperature to 58°. With continued heating, boiling was rapid at 58° and a gas which evolved was collected in a dry-ice/acetone trap connected in the exit line. Within 2 h from the start of gas evolution the residue in the reaction vessel had become noticeably viscous and the gas evolution had slowed.

After 18 h at 60–80° the residue was quite viscous and weighed 81.1 g after filtration. Viscosity 2348 cs.; $n_D^{25}$ 1.4034. {Found: H(Si), 0.021 [$Hg(OAc)_2$]; H(OSi), 0.047 % (Karl-Fischer).}

The volatile compound collected in the cold trap was identified as dimethylsilane by comparative infrared analysis with a known standard. The dimethylsilane collected weighed 51.0 g (85 % of theoretical) b.p. at atm. −22 to −20°.

*Sealed-tube technique (experiments are summarized in Table* 1)

Reactions at 110° and those of a survey nature were performed in sealed capillary tubes (Sargent S-44846-B2). The contents of the tubes were analyzed by gas–liquid chromatography (GLC) using a special apparatus adapted from a F and M Model® S1-4 solid sample injector (F and M Division, Hewlett Packard), which allowed the sealed reaction capillaries to be broken inside the sealed injection port of the gas chromatograph (F and M Model 500). The column used for the analysis was 10′ × 1/4″ stainless steel tubing packed with 20 % Dow Corning® FS-1265 fluid on 80 mesh chromosorb W. The retention time for dimethylsilane on this column at 50° was approximately 90 seconds at a helium flow rate of 50 cc per min.

Toluene (5 % by total weight of sample) was used as a convenient internal standard for the conversion of the recorded peaks from area percentages to weight percentages and mole percentages (which allowed the calculation of percent conversion).

The general procedure consisted of loading the capillary tube with approximately 3 mg (5–10 mm in bottom of tube) powdered clay or silica–alumina. The tube and catalyst were heated at 150° for 1–2 h to drive off any adsorbed water. The tube was cooled to −78°, and 15 $\mu$l of siloxane-internal standard mixture was added by means of a 50 $\mu$l syringe. The tube was sealed at the proper length and heated in an oven at 110° for 24 h. After this reaction period the tube was mounted in the injection apparatus and injected into a cool position in the gas chromatograph (35°). After the instrument had reached equilibrium (30–45 sec) the tube was broken by pressing it against the back of the heated injection block (300°). The volatile materials were immediately vaporized and the broken glass, catalyst and other non-volatile residue were automatically removed when the apparatus was withdrawn from the injection port. The column was held at 50° until the volatile silane was eluted and then the temperature was programmed to 300° at 15° per min in order to remove higher boiling materials from the column. A large area or weight percent volatile silane was considered an indication of a high degree of conversion. Because of the long reaction time, the degree of conversion was taken as a crude measure of the catalyst activity.

The identities of the various products listed in Table 1 were confirmed by comparative GLC and/or infrared analysis (of GLC purified samples) with known specimens.

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## SUMMARY

Naturally occurring clays and silica–alumina are unique acid catalyst for the exchange of hydrogen and siloxy ligands on silicon. The interchange of ligands is reversible and intermolecular with a tendency for like ligands to accumulate on the same silicon. The reactivity of various catalysts with hydride functional siloxanes are summarized, and possible reaction mechanisms are suggested.

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