

## Infrared Study of Reaction Between Alkoxysilanes and Silica

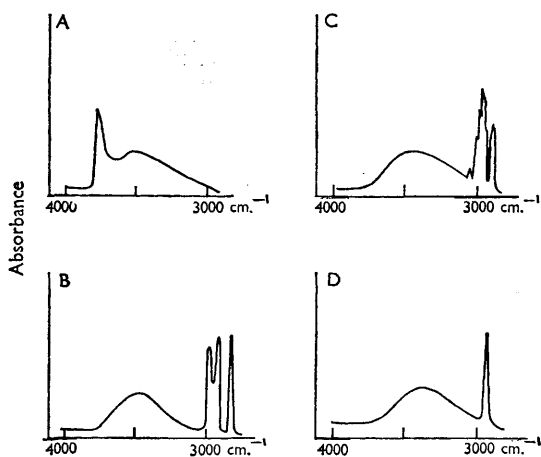
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WHILE trimethoxysilanes are widely used for adherence of polymers to glass, the nature of the interfacial bonding to glass remains unknown.<sup>1</sup>

We now present evidence that a siloxane bond (Si-O-Si) is formed between a trimethoxysilane and amorphous silica.

Infrared examination (Fig. 1; curve A) of high surface silica ( $\sim 200 \text{ m.}^2/\text{g.}$ ) dried at  $500^\circ\text{C}$  showed a strong adsorption band at  $3715 \text{ cm.}^{-1}$  assigned to the OH stretching frequency of essentially free SiOH surface groups.<sup>2</sup> The dried silica was refluxed with 0.012–0.022M-toluene solutions of the silanes  $[\text{RSi}(\text{OMe})_3]$  where  $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2$  or  $\text{CH}_2\text{O}\cdot\text{CH}\cdot\text{CH}_2\text{O}\cdot[\text{CH}_2]_3\cdot$ , filtered, and dried at  $150^\circ$ . The infrared spectra of the treated silicas (Fig. 1; curves B and C) show eradication of the silanol band. Both spectra also exhibit C-H stretching bands around  $2900 \text{ cm.}^{-1}$ , further substantiating the existence of the silane on the silica. Treatment of dried silica with toluene, methanol, or propanol, the last two representing excellent hydrogen-bonding agents, did not materially alter the location or intensity of the silanol band. The spectra of the alcohol-treated silica did have C-H stretching bands indicating their presence on the silica. When chloride was substituted for the methoxys, *i.e.*,  $\text{Cl}_3\text{SiMe}$ , the silanol surface groups were removed (Fig. 1; curve D).

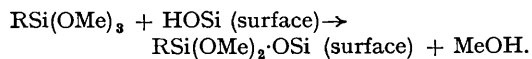


Infrared spectra of various materials on silica of high surface area: A, silica alone; B, methyltrimethoxysilane; C, allyltrimethoxysilane; D, methyltrichlorosilane.

<sup>1</sup> K. A. F. Schmidt, *Glastech. Ber.*, 1964, **37**, 1.

<sup>2</sup> T. H. Elmer, I. D., Chapman and M. E. Nordberg, *J. Phys. Chem.*, 1962, **66**, 1517.

This evidence leads to the conclusion that trimethoxysilanes react, under these conditions, with surface silanol groups by some mode other than hydrogen bonding. Probably the reaction is a condensation to yield a siloxane bond:



The similar reaction of an alkylsilanol with an

alkoxysilane to yield a siloxane bond has been previously reported.<sup>3</sup>

The adsorption bands at 2950  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  present in the methyltrimethoxysilane (curve B) and absent from methyltrichlorosilane (curve D) indicates that there are methoxy-groups either adsorbed on the surface or unchanged. Exposure to water readily removes the methoxy-groups.

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<sup>3</sup> B. Smith, *Svensk Kem Tidssk.*, 1955, **67**, 421.