

## MIR Spectroscopy: A New Method for Studying the Hydrolysis of Hexamethylcyclotrisilazane in Air\*

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### Synopsis

A new method for studying the rate of hydrolysis of hexamethylcyclotrisilazane has been developed. This method, MIR spectroscopy in the infrared region of 4000–625  $\text{cm}^{-1}$ , was employed to characterize the reactions. The change in relative intensity of characteristic bands of the reactant is plotted as a function of time to give the required rate curves. The effects of temperature, pressure, exterior magnetic fields, and ultraviolet-visible radiation on the rate curves are also discussed.

### Introduction

As part of an exploration of new methods of synthesizing silicon-nitrogen oligomers and polymers, the present work was undertaken to develop a direct method for studying the hydrolysis of silicon-nitrogen bonds. Infrared spectroscopy was chosen as the technique to characterize the reactions to be studied because the absorption bands of the reactants and products are strong and sharp, well-known, and relatively close together.

Silicon-nitrogen polymers and many oligomers cannot be readily prepared for scanning in the infrared region by such conventional techniques as mulling with Nujol; pressing into potassium bromide, cesium bromide, and cesium iodide disks; and smearing onto sodium chloride plates. These oligomers and polymers scatter radiation extensively and deteriorate under high pressures. More important, the spectra of both the silicon-nitrogen compounds and the water vapor are obtained simultaneously with transmission techniques. Under these conditions, several spectral bands from the reactants and products overlap, and interfere with one another. These difficulties can be overcome with the multiple internal reflectance (MIR) technique.

The MIR technique permits the characterization of liquids and solids (not of gases) by infrared spectroscopy with a minimum of sample preparation.<sup>1-3</sup> Infrared energy is so focused onto the end of an infrared-transmitting plate that the incident beam is totally reflected internally several hundred times. The electric field of the reflected waves penetrates many

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times into the sample, which has been placed in contact with the surface of the plate. The electric field is frustrated by the sample at characteristic frequencies, and a plot of the unfrustrated (transmitted) radiation versus frequency gives a curve nearly identical to a conventional, infrared transmission spectrum. All the bands in ordinary transmission spectra are present in MIR spectra, and have approximately the same shapes and relative intensities. Consequently, the identity of substances can be determined by comparing their MIR spectra with transmission spectra of known materials. In addition, these substances can be identified, with minor corrections for slight band displacements and dispersion in the vicinity of the absorption bands, by group correlation analysis.

### Experimental

The MIR spectra in this study were obtained by spreading a uniform layer of hexamethylcyclotrisilazane (Chemicals Procurement Laboratories, Inc., College Point, New York) on the surface of a  $50 \times 20 \times 2$  mm KRS-5 plate. The coated plate was placed in the especially constructed sample holder shown in Figure 1. This sample holder has two cavities in which the atmosphere surrounding the samples can be controlled. Dried air, air at various temperatures, and air that contains known amounts of water vapor can be pumped through these cavities. This arrangement is very convenient because the environment of the sample can be changed without disturbing the sample. A Teflon sample holder (Fig. 2) was also used for these studies, to expose the hexamethylcyclotrisilazane which was coated on an MIR plate to the humidity of our laboratory air, and to study the

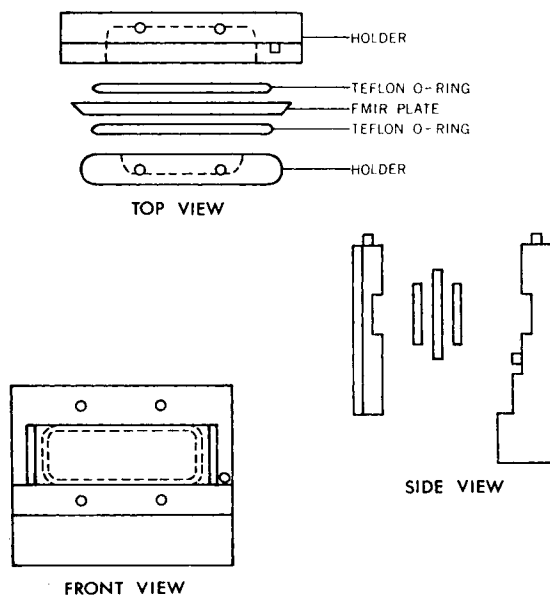


Fig. 1. MIR controlled atmosphere sample holder.

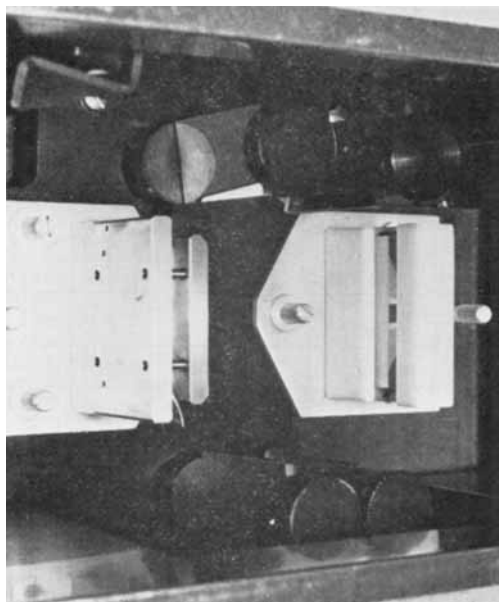


Fig. 2. Teflon sample holder.

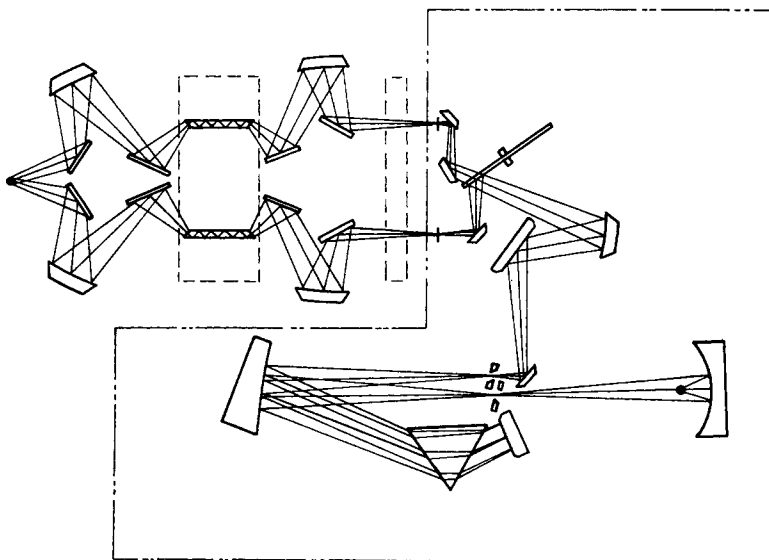


Fig. 3. Optical system for MIR.

effects of irradiation of the samples by ultraviolet-invisible light and high magnetic fields. The assemblies were inserted into the sample beam of a Wilk's Model 8B internal-reflection spectrophotometer (Wilk's Scientific Corporation, South Norwalk, Connecticut). An uncoated assembly was

placed in the reference beam of the optical system (Fig. 3), to balance the optical paths, and the samples were scanned in the region  $1300\text{--}700\text{ cm}^{-1}$  every 4–15 min.

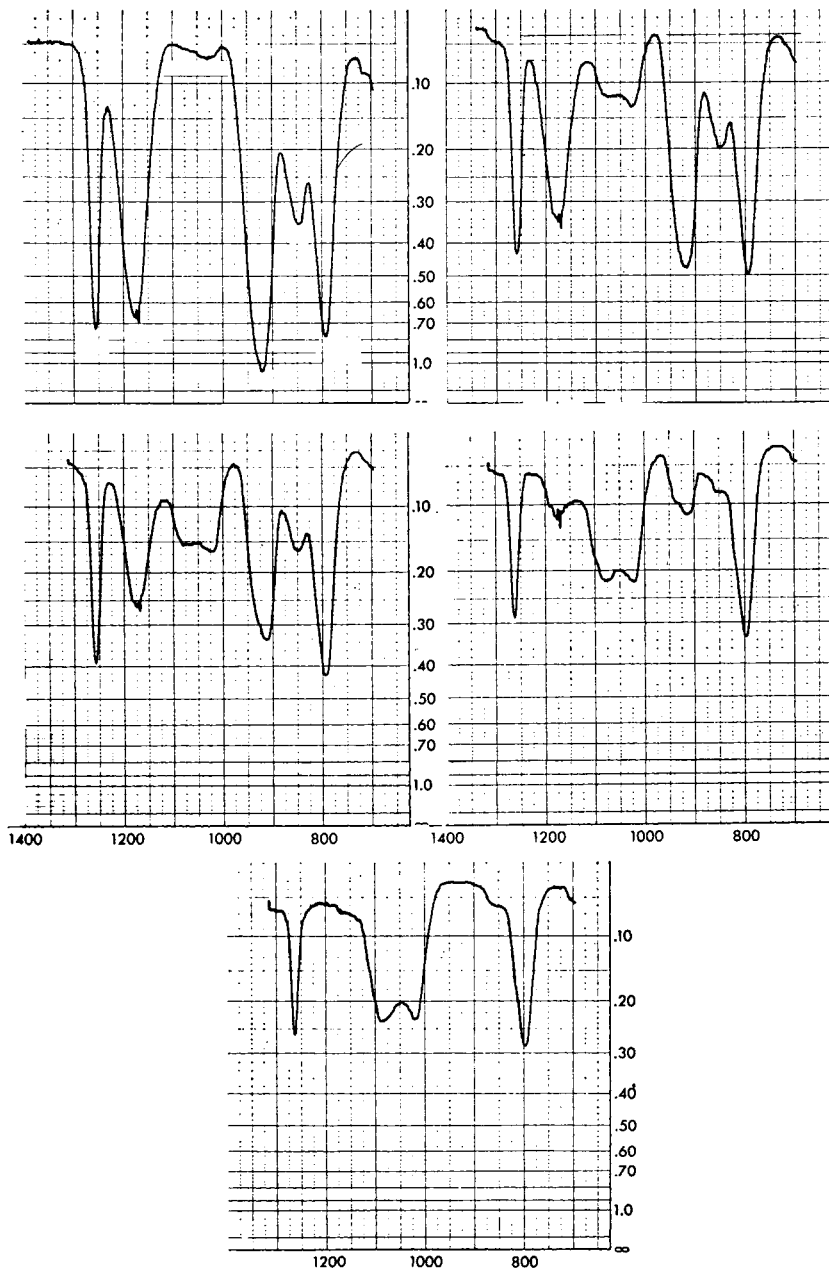


Fig. 4. MIR spectra of hexamethylcyclotrisilazane during hydrolysis.



were hydrolyzed; and the intensity of the bands near 1075 and 1030  $\text{cm}^{-1}$  increased because of the formation of Si—O bonds during hydrolysis. These changes in the infrared spectra of hexamethylecyclotrisilazane are shown in Figure 4. The areas of each of these bands were determined with a planimeter, and the areas of the bands near 1180, 1075, 1030, and 920  $\text{cm}^{-1}$  were divided by the areas of the bands at 1260 and 790  $\text{cm}^{-1}$ . These quotients were then plotted as a function of time (Fig. 5). Any one of these curves can be employed to determine the rate of hydrolysis of hexamethylecyclotrisilazane in air.

Several parameters that affect the rate of hydrolysis were also investigated with this technique. Such parameters as the external magnetic field and ultraviolet irradiation did not affect the rate of hydrolysis, but changes in concentration of environmental water vapor, temperature and atmospheric pressure did affect the rate of hydrolysis of hexamethylecyclotrisilazane. By increasing the concentration of water, by raising the temperature, and by lowering the pressure, the rate of hydrolysis was increased.

An advantage of this technique over others is the small amount of material required for these characterizations. The MIR technique can, if necessary, be used to obtain the spectra of less than 5  $\mu\text{g}$  of material. The spectra shown in Figure 4 were obtained with approximately 50  $\mu\text{g}$  of hexamethylecyclotrisilazane. Also, reactions that take place on the surface of other materials can be studied without the reactants being removed from their substrate.<sup>3</sup>

The MIR technique, as described in this paper, cannot be employed to obtain quantitative rate data for calculation of rate constants and activation energies because (1) the system is not homogeneous with respect to the infrared radiation and (2) other parameters, such as the water–solid interfacial area, film thickness, diffusion rates of reactants and products with the film, and the absolute concentration of the reactants, were not studied in detail.

The results of these experiments suggest that the MIR technique can be successfully used to detect induced chemical changes and to characterize their rates of reaction.

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