Spectra and Structure of Silicon-Containing Compounds. XXVIII1 Infrared and Raman Spectra, Vibrational Assignment, and Ab Initio Calculations of Vibrational Spectrum and Structural Parameters of Vinyltrichlorosilane

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Received July 28, 2000; accepted August 29, 2000

The infrared spectra (3200-50 cm⁻¹) of gaseous and solid vinyltrichlorosilane, CH₂=CH-SiCl₃, have been recorded. In addition, the Raman spectrum (3200-10 cm⁻¹) of the liquid has been recorded and quantitative depolarization values obtained. The infrared spectrum of the sample dissolved in liquid xenon (~ 80 °C) has also been recorded. Using the experimental data and normal coordinate calculations with scaled ab initio force constants, the complete vibrational assignment is proposed. The torsional mode was observed in the infrared spectrum of the gas at 69 cm⁻¹ and the threefold barrier of internal rotation was calculated to be 500 cm⁻¹ (5.98 kJ/mol). Ab initio calculations have been carried out at the restricted Hartree–Fock level of the theory as well as with full electron correlation by the perturbation method to second order with different basis sets up to 6-311+G(d,p) to obtain the optimized geometries, harmonic force constants, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies. The ab initio predicted structural parameters are compared with those obtained from a previous electron diffraction study.

KEY WORDS: Infrared and Raman spectra; ab initio calculations; structural parameters; vinyltrichlorosilane.

INTRODUCTION

For quite some time we have been interested in the molecular structure, conformational stabilities, barriers to internal rotation, and the thermodynamic properties of several series of organosilicon compounds. We have investigated a number of these molecules which contain a vinyl group attached to the silicon atom [1–8] with the general formula CH₂CHSiX₂Y, where X = H, Cl, F, and CH₃ and Y = H, Cl, F, and CH₃. In many of these studies, we have obtained the conformational stabilities and structural parameters, which were compared to those obtained from ab initio calculations. We also compared the results with some of the corresponding carbon analogs.

Since the chlorine atom and the methyl group have essentially the same size, differences in the structural parameters and conformational stabilities of the molecules with the general formula CH₂=CHSiCl(CH₃)₃−ₙ can probably be attributed to the electronegativity. Therefore, we carried out conformational stability studies of CH₃CHSiCl(CH₃)₂ [7] and CH₂CHSiCl₂CH₃ [6] to determine the effect of the electronegativity by assuming the steric effect due to the size of the substituent is negligible. The results of these studies indicated that the methyl group has a preference for eclipsing the double

1For part XXVII, see Spectrochim. Acta 56A 2000 1957.
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bond. For methylvinyldichlorosilane [6] the cis conformer is the more stable form by 77 ± 8 cm\(^{-1}\) (0.92 ± 0.10 kJ/mol), whereas for dimethylvinyldichlorosilane [7] the gauche conformer is the more stable rotamer by 41 ± 9 cm\(^{-1}\) (0.49 ± 0.11 kJ/mol). For both of these molecules, vibrational assignments were proposed for both conformers and the structural parameters predicted from \textit{ab initio} calculations. As a combination of these studies, we have carried out a vibrational and \textit{ab initio} study of the trichloride, \textit{i.e.}, vinyltrichlorosilane, CH\(_2\)CHSiCl\(_3\).

There is only limited vibrational spectroscopic information on vinyltrichlorosilane. The analyses of the normal vibrations were reported by Khristenko and Pentin [9]. There has also been some MO-LCAO-SCF calculations at the level of CNDO/2, where there was interest in the intensity of the C=C stretch [10] and the low-frequency spectra (infrared and Raman) were obtained to propose group frequencies for the SiCl\(_3\) moiety [1]. Rogers and Kalasinsky [11] reported the infrared spectrum of gaseous vinyltrichlorosilane along with a vibrational assignment at an International Conference on Fourier Transform Infrared Spectroscopy. There has also been an electron diffraction study [12] from which only very limited structural information was obtained. Therefore, we have carried out an infrared spectral investigation of the gas, xenon solution (−80°C), and solid, along with a Raman investigation of the liquid and solid. In addition, we have carried out \textit{ab initio} calculations at the restricted Hartree–Fock level of the theory as well as with full electron correlation by the perturbation method to second order [13] with different basis sets up to 6-311+G(d,p). From these calculations, we obtained the optimized geometries, harmonic force constants, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies for vinyltrichlorosilane. The results of this spectroscopic and theoretical study are reported herein and compared to the corresponding quantities for some similar molecules.

**EXPERIMENTAL**

The sample of vinyltrichlorosilane was purchased from Aldrich Chemical Co., (Milwaukee, WI). Purification was accomplished using a low-temperature, low-pressure fractionation column.

The mid-infrared spectra (Fig. 1) of gaseous and

![Fig. 1. Comparison of experimental and calculated infrared spectra of trichlorovinylsilane: (A) observed infrared spectrum in the gas phase; (B) observed infrared spectrum in the solid phase.](image)