Conformational stabilities of CH 2CHSi(CH 3) n X 3 − n (X=F and Cl) from variable temperature FT–IR spectra of rare gas solutions

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Conformational stabilities of $CH_2=CHSi(CH_3)_nX_{3-n}$ (X = F and Cl) from variable temperature FT-IR spectra of rare gas solutions

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Abstract

Variable temperature (-105 to $-150°C$) studies of the infrared spectra ($3500-400$ cm^{-1}) of methylvinyldifluorosilane, $CH_2CHSiF_2CH_3$, dimethylvinylfluorosilane $CH_2CHSiF(CH_3)_2$ and methylvinyldichlorosilane, $CH_2CHSiCl_2CH_3$, dissolved in liquid krypton have been recorded. The enthalpy difference of methylvinyldifluorosilane has been determined to be 53 ± 11 cm^{-1} (0.64 ± 0.13 kJ/mol) with the *gauche* conformer the more stable form. However in the crystalline solid only the *cis* conformer is present. For the corresponding dichlorosilane the enthalpy difference has been determined to be 46 ± 20 cm^{-1} (0.55 ± 0.24 kJ/mol) with the *cis* conformer more stable. For dimethylvinylfluorosilane the enthalpy difference has been determined to be 32 ± 7 cm^{-1} (0.38 ± 0.08 kJ/mol) with the *gauche* conformer the more stable form. Ab initio calculations have been carried out with several different basis sets up to MP2/6-311 + G(2d,2p) with full electron correlation by the perturbation method for all three of the silanes from which the conformational stabilities have been determined. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

We [1–8] have been determining the conformational stabilities of some similar silicon compounds to the 3-halopropenes such as $CH_2CHSiX_3Y_n$ where X and Y may be H, F, Cl, Br and CH_3. For methylvinylsilane in the liquid state, the enthalpy differences of 254 ± 16 cm^{-1} (3.04 ± 0.19 kJ/mol) and 231 ± 17 cm^{-1} (2.76 ± 0.20 kJ/mol)

have been reported [4,9] with the *cis* conformer being the more stable rotamer although a much smaller value of 84 cm^{-1} (1.00 kJ/mol) was initially reported [10]. However, from the temperature studies of the infrared spectra of krypton solutions [11], the *gauche* conformer was determined to be the more stable rotamer with an enthalpy difference of 133 ± 11 cm^{-1} (1.59 ± 0.13 kJ/mol).It is expected that the stability in the gas phase will be very similar to that found in the krypton solution [12–16]. It is well known that the conformer which is stable in the liquid may not be the form that is the more stable rotamer in the vapor state, particularly if the stable conformer in the liquid has a relatively large dipole moment compared to that for the other form. In our previous [7] study of methylvinyldifluorosilane
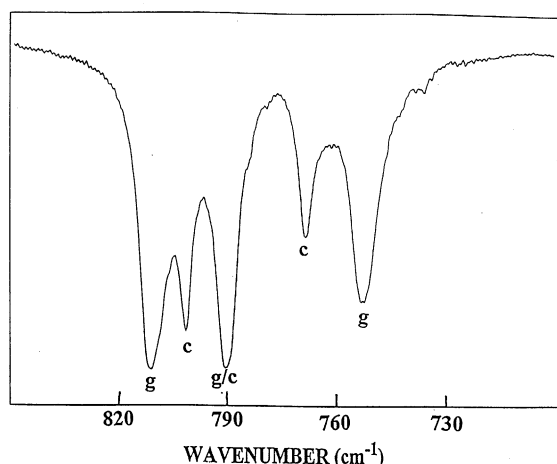
Fig. 1. Infrared spectrum of a krypton solution of MVDCS with the assigned conformer peaks indicated (*g = gauche*;   *c = cis*).

determined the experimental gas-phase composition to be 35–65 (±41)% for the *cis* to *gauche* ratio with an estimated conformational energy difference of 0.0 ± 1.2 kcal/mol (0 ± 420 cm^{-1}). Since these uncertainties are so large it is clear that the conformational stability in the gas phase have not yet been determined. Therefore we have carried out a variable temperature study (-105 to $-150°$C) of MVDFS with the sample dissolved in liquid krypton. Similar studies have also been carried out for dimethylvinylfluorosilane (DMVFS) and methylvinyldichlorosilane (MVDCS). We have also carried out ab initio calculations with much larger basis sets than previously used [7,17] to predict the conformational stability.

2. Experimental

The sample of MVDCS was purchased from Aldrich Chemical Co., Milwaukee, WI. The sample of MVDFS was prepared from the corresponding chloride by fluorination using freshly sublimed antimony trifluoride. The sample of DMVFS was prepared by the reaction between the chloro derivative, $CH_2=CH(CH_3)_2SiCl$, and freshly sublimed antimony trifluoride at room temperature without solvent for one hour. The samples were purified at a low temperature, low pressure fractionation column and the purity was checked by mass spectrometry and NMR data.

The mid-infrared spectra (Fig. 1) of the three samples dissolved in krypton as a function of

(MVDFS), we utilized the relative intensity at room temperature of three conformer pairs to estimate the amounts where the assignment of the individual bands was based on the ab initio predicted frequencies. Since all of the assigned *gauche* bands for the three conformer pairs were stronger than the corresponding *cis* bands it was concluded that the *gauche* conformer was the predominant form in the fluid phases. Since the gauche form has two equivalent conformers, this rotamer could be the predominant form but not be the most stable conformer in the fluid phases, i.e. greater than 50% abundance but less than 67%. In a recent electron diffraction study of MVDFS the authors [17]

Table 1
Temperature and intensity ratios for conformational study of MVDFS, MVDCS, and DMVFS determined from krypton solution

| T(°C)	K	MVDFS I_{975g}/I_{971c}	$-\ln K$	MVDCS I_{752g}/I_{768c}	$-\ln K$	DMVFS I_{962g}/I_{965c}	$-\ln K$
-105	5.95	0.6992	0.3578			2.5385	-0.9316
-110	6.13	0.7889	0.2371	3.8415	-1.3459	2.7410	-1.0083
-115	6.32	0.7930	0.2319	3.7240	-1.3148	2.7051	-0.9951
-120	6.53	0.8028	0.2197	3.8208	-1.3405	2.8240	-1.0382
-125	6.75	0.8189	0.1998	3.1830	-1.1578	2.7941	-1.0275
-130	6.99	0.8509	0.1615	3.3491	-1.2087	2.8300	-1.0403
-135	7.23	0.8343	0.1812	3.2928	-1.1917	2.7710	-1.0192
-140	7.51	0.8618	0.1487	3.4348	-1.2340	2.8501	-1.0473
-145	7.80	0.8512	0.1611	3.3100	-1.1970	2.8876	-1.0604
-150	8.12	0.8753	0.1332	3.3676	-1.2142	2.9420	-1.0791
ΔH			53 ± 11 cm^{-1}		46 ± 20 cm^{-1}		32 ± 7 cm^{-1}
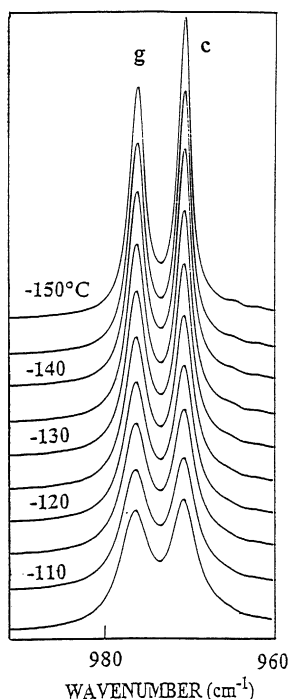
Fig. 2. Temperature dependence of the ratio of *gauche* to *cis* conformers for krypton solution of MVDFS.

temperature were recorded on a Bruker model IFS 66 Fourier transform interferometer equipped with a Globar source, a Ge/KBr beamsplitter and a DTGS detector. The spectra were recorded at variable temperatures ranging from -105 to $-150°C$. All the spectra were collected with 100 scans at a resolution of 1.0 cm^{-1}. The temperature dependent spectral data for the conformer bands are listed in Table 1 for krypton solution.

3. Results and discussion

From ab initio predications, confident assignments for the normal vibrations for both the conformers of MVDFS were obtained. Attention was then turned to obtaining the relative stability of the two rotamers. Since only small interactions are expected to take place between the noble gas atoms and the dissolved compound, the fundamentals are expected to only shift slightly compared to the wave numbers for the corresponding modes in the infrared spectrum of the

gas. Furthermore, the absorption bands for the two conformers are frequently resolved in the infrared spectra of the rare gas solutions compared to those in the infrared spectra of the gas. The infrared spectra of the pair of bands at 975*g*/971*c* (Fig. 2) where *g* and *c* indicate *gauche* and *cis* bands, respectively, were recorded over the temperature range from -105 to $150°C$ from the krypton solution. The area intensities of each conformer pair were fit to the equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where K is the area ratio I_g/I_c. It is assumed that the ΔH value is not a function of temperature over the range used in this study. Using a least square fit and from the slope of the line, the determined ΔH is 53 ± 11 cm^{-1} with the *gauche* conformer the more stable rotamer. This value is expected to be near the values for the gas [12–16] since the size and dipole moments of the two conformers are nearly the same.

Variable temperature studies of the infrared spectra of DMVFS dissolved in liquid krypton were also conducted to determine the enthalpy difference between the two stable conformers of this molecule. The spectral changes in liquefied krypton of the pair of the bands at 962*g*/965*c* cm^{-1} are shown in Fig. 3. From all spectral data from liquefied krypton solution,
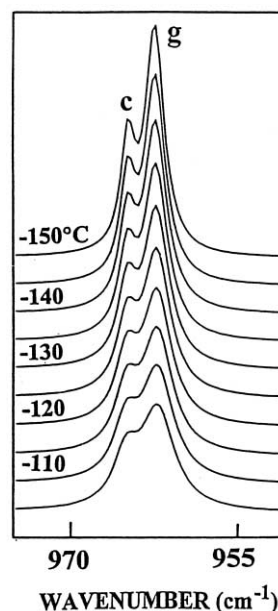

Fig. 3. Temperature dependence of the ratio of *cis* to *gauche* conformers for krypton solution of DMVFS.

we observed increases in the intensity of the infrared bands assigned to the *gauche* conformer as the temperature decreased. This clearly confirms the stability of the *gauche* rotamer over the *cis* conformer in this rare gas solution. In order to obtain the enthalpy difference, ten spectral data points were obtained over the temperature range from -105 to $-150°C$ for the krypton solution. The intensities of the conformer pair were fit to the equation $-\ln K = (\Delta H/RT) - (\Delta S/R)$, as indicated previously. Using a least squares fit of the slope of the line, a ΔH value of 32 ± 7 cm^{-1} was obtained with the *gauche* conformer the more stable form.

Similarly, conformer doublets were observed in the vibrational spectra of MVDCS. Bands observed at $752g$ and $768c$ cm^{-1} in the infrared spectrum of the krypton solution were used to obtain the enthalpy difference for these molecules. From the least squares fit and the slope of the line, the ΔH value was found to be 46 ± 20 cm^{-1} with the *cis* conformer the more stable rotamer.

From the MP2/6-311 + G(d,p) calculations the *cis* conformer was predicted to be more stable for both the fluorides by 10 cm^{-1} which is at variance with the experimental results. However, this value is very small so it cannot be expected to predict the conformerational stability. For the chloride, the ab initio MP2 calculations predict the correct conformer stability. It is interesting that for the difluoride molecule the fluorine atom is eclipsing the double bond whereas for the monofluoride, the methyl group is eclipsing the double bond. The difference is probably due to the significant decrease in the silicon to carbon distance of the vinyl group. The corresponding chloride molecules are not expected to have this alteration since the chlorine atom is not expected to have such a profound effect on the carbon silicon distance.

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