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VIBRATIONAL SPECTRA OF SOME SUBSTITUTED TRIVINYLSILANES

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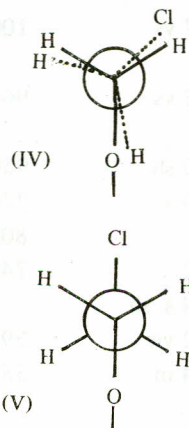
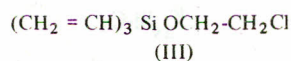
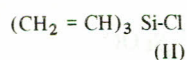
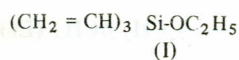
The preparation of trivinylethoxysilane (I), trivinylchlorosilane (II) and trivinyl (2-chloroethoxy) silane (III) and the assignments of various group frequencies of their vibrational spectra are reported. It has been suggested that twisting (γ_{as}) CH_2 mode of vibration can be used to differentiate ethoxy group from 2-chloroethoxy group in technical silicon products.

Key words: Vibrational, Spectra, Trivinylsilane.

INTRODUCTION

Vinylsilanes have acquired technical importance in a number of different ways e.g. reactive sites can be created by incorporating vinylsilane units in the organic polymers where crosslinking can readily be initiated. The reactivity of alkenyl group on silicon atoms has long been utilized in silicon-rubber technology. The possibility of co-polymerization with unsaturated organic compounds has also aroused interest [1] at various times. The ability of hydrogen atom of silanes to add to the vinyl group of vinylsilanes promoted by platinum catalysts has acquired technological importance [2]. Vinyl and allylsilanes undergo further reaction well known to organic chemists [3].

Although a number of vinylsilanes are encountered in various communications [4-6] only a little information about the preparation of vinylsilane monomers of general formula $(\text{CH}_2 = \text{CH})_3 \text{Si-x}$ (where $x = \text{Cl}, \text{OC}_2\text{H}_5, \text{OC}_2\text{H}_4\text{Cl}$) is available. Furthermore their vibrational spectra have not been studied systematically. In this article we report the preparation and some physical properties of some vinylsilanes monomers in glc pure form. Infrared, far infrared and laser Raman spectra of the silanes from these series have also been studied.



EXPERIMENTAL

Silanes were prepared [6,7] to glc grade of purity as follows.

Preparation of trivinylethoxysilane (I). A solution of vinyltriethoxysilane (47.5 g, 0.25 mole), in dry tetrahydrofuran (400 ml) was added in a three-necked one-liter flask fitted with a cold water condenser, an efficient stirrer and a dropping funnel. Dry nitrogen was flushed to remove air from the reaction vessel. Vinylmagnesium bromide (65.5 g, 0.50 mole) was added slowly from the dropping funnel with rapid stirring of the reaction mixture. The reaction mixture was refluxed for three hours. Tetrahydrofuran was then distilled off at atmospheric pressure and residue was subjected to vacuum distillation. Further fractionation of the distillate by Buchi distillation column at reflux ratio of 1:15 yielded few ml glc pure divinyl-diethoxysilane and tetravinyl silane were obtained in addition to the main produce of trivinylethoxysilane, b.p. 132.5° , d_{20} 0.8451 g/ml n_D^{20} 1.4381, molar refraction theoretical: 48.190, practical 47.84.

Preparation of trivinylchlorosilane (II). A mixture of trivinylethoxysilane/benzoylchloride (30 ml) and anhydrous aluminium chloride (0.385 g) was warmed to 40° with continuous stirring for six hours. Completion of the reaction was followed by glc. Crude trivinylchlorosilane (II) was separated from the reaction mixture by distillation under reduced pressure. The crude product was purified by fractionation through a Buchi column at reflux ratio of 1:10 b.p. 122° , d_{20} 0.9506, n_D^{20} 1.4616, molar refraction theoretical 42.30 practical; 41.87.

Preparation of trivinyl (2-chloroethoxy) silane (III). A mixture of trivinylethoxysilane (3.64 ml, 0.02 mole) and ethylenechlorohydrine (1.6 ml, 0.02 mole) was added in 50-ml round bottom flask fitted with a cold water condenser and placed on a magnetic stirrer/hotplate. The contents were stirred and refluxed with continuous disti-

llation of ethanol. The aliquot portions of the reaction mixture were withdrawn from time to time and analysed by glc to follow the reaction. The reaction was stopped when whole of the ethylenechlorohydrine was used up and distilled to 95% glc pure (III), b.p. 181^o, n_D²⁰ 1.4653.

Infrared spectra were taken in the range from 4000-400 cm⁻¹ using -KBr window on DIGLLAB FTS-14 interference type spectrophotometer. Far-infrared spectra were recorded on Beckman FS-720 far-infrared interferometer in the range from 40-400 cm⁻¹ using polyethylene window in liquid film or as *n*-hexane solution. Laser Raman spectra were measured in a special 0.5 ml liquid sample holder on Cary-82 Raman spectrometer with the excitation of the blue line of Argon laser under 100-150 mv reduced power.

RESULTS AND DISCUSSION

The assignments of the observed infrared and Raman frequencies of compounds (I)-(III) are given in Tables 1,2,

and 3 respectively. Our assignments for vinylgroup frequencies are in accordance with the reported [8-15] values for vinyl group in similar compounds.

The salient features of the spectrum of (I) is that ethyl group frequencies are intermixed with some of the vinyl group vibrations whereas in the spectrum of (II) all the characteristic vibrations of the vinyl group have been assigned conveniently. $\nu_{C=C}$ stretching vibrations of compounds (I), (II) and (III), have been found around 1594 cm⁻¹ - 1600 cm⁻¹ practically unaffected by the nature of the groups attached to silicon atom. Close examination of spectrum of (I) and (II) shows that the twisting (γ_{as}) CH₂ vinyl and rocking (β_{as}) CH₂ vibration are overlapped in the spectrum of ethoxy compound where as in 2-chloroethoxy derivative a separation of 30 cm⁻¹ is observed in these vibrations. This criteria can be used for identification and quantitative evaluation of chloroethoxy silanes from ethoxy silanes in technical silicon products. Further comparison of the spectra of (II) and (III) reveals

Table 1. Assignment of the infrared and Raman frequencies of trivinylethoxysilane (1).

Infrared	Raman	Assignments	Infrared	Raman	Assignments
3184 vw	3180 m,p	2 x $\nu_{C=C}$	1483 vw	1482 vw, dp	(Et)
3043 s	3060 s, dp	$\nu_{as}CH_2$		1456 vw, dp	$\delta_{as}CH_3$ (Et)
3010 m	3013 w, p	$\nu_{C=C} + \beta_sCH_2$	1445 vw	1445 vw, dp	δCH_2 (Et)
2974 vs	2977 vs, p	ν_{CH}, ν_{CH} (Et)	1405 vs	1405 vs, p	β_sCH_2
2950 s	2950 m, p	ν_sCH_2	1394 s		δ_sCH_3 (Et)
2908 m	2929 vs, p	ν_{CH} (Et)	1365 sh		
2900 m		ν_{CH}, ν_{CH} (Et)	1295 vw		γ_sCH_2 (Et) wagging
2876 m	2880 p	$\nu_{C=C} + 2 \delta_{as}CH_3$	1273 w	1274 vs, p	βCH
	2805		1164 s		$\gamma_{as}CH_2$ (Et)
2770 vw	2767 vw, p	2 $\delta_{as}CH_3$	1106 vs	1103 w,p	$\nu_{as}SiOC$ coupled with CC of Etgr.
2730 vw	2729 w, sh,p	(Et)	1084 vs	1086 w,p	
2688 vw					
2630 vw			1007 vs	1008 w,dp	$\gamma_{as}CH_2, \beta_{as}CH_2$
2435 vw					
2410 vw			962 vs	964 vw, dp	$\gamma_sCH_2, \delta CH_3$ (Et)
2350 vw					
2270 vw		$\gamma_{as}CH_2 + \beta CH$	950 sh	950 sh	
2180 vw			769 s	770 w,p	ν_sSi-OC
2142 vw				808 vw	
2003 vw		2x $\beta_sCH\lambda_2$	732	740 vw, dp	$\nu_{as}Si-C_3$
		2x $\gamma_{as}CH_2$	724 s, sh		
1924 w		2x γ_sCH_2	602 vw	599 s,p.	
1865			554 m	555 sh,p	ν_sSiC_3 (Confor- mation)

(Continued)

(Table 1, continued)

1714 vw			542 m,sh,	545 sh,dp	γ CH
1594 s	1594 vs, p	ν C=C	317 w,b	390 w	δ Si-CC
			278 m	278 vw	
			225 w,b		δ SiC ₃
				174 vw,dp	
			115		δ Si-OC
			70	67	τ Si C=C

w, m, s = weak, medium strong, v = very, p = polarized, dp = depolarized, sh = shoulder. Approximate description of normal modes and their notation is as follows; C=C stretching ν C=C, CH stretching ν CH, asymmetric stretching ν_{as} , symmetric stretching ν_s , CH₂ scissor-

ing β_s , CH₂ rocking β_{as} CH₂, in plane deformation β , out of plane deformation γ , skeletal deformation δ , CH₂ twisting γ_{as} , CH₂ wagging γ_s , asymmetric δ_{as} , symmetric deformation δ_s , CH₂, CH₃, rocking mode δ (CH₃).

Table 2. Assignment of the infrared and raman frequencies for trivinylchlorosilane (II)

Infrared	Raman	Assignments	Infrared	Raman	Assignments
3184 w	3184 w,p	2x ν C=C	802 vw		
3059	3064 m,dp	ν_{as} CH ₂	734 vs		ν_{as} SiC ₃
3016 s	3016 w,p	ν C=C + β_s CH ₂	648 vs		ν_s SiC ₃
2980 s	2985 v,s,p	ν CH	625 sh		
2950 s	2958 m,p	ν CH ₂	580 m,sh	580 dp	Impurity
2850 vw	2846 w	ν C=C + 1270	550 s	553 dp	γ CH
2800			470 s	470 s,p	ν SiCl
2672 vw		β_s CH ₂ + β CH	360		
2340				338 p	δ SiCC
2268 w			315 w	315 w	
2150 vw		γ_{as} CH ₂ + β CH	195 m	195 w,dp	δ_{as} SiC ₃
1998 w		β CH + ν_{as} SiC	120 vw	150 p	δ_s SiC ₃
1932 m		2 x γ_s CH ₂	70 vw		τ SiC=C
1778 w					
1720 w					
1597 vs	1598 vs,p	ν C=C			
1453 w					
1470 vs	1406 vs,p	β_s CH ₂			
1316 m	1355 w,p	1003 + 315			
1270 w	1270 vs,p	β CH			
1205 w	1210 vw,p				
1174 w					
1064 s		Impurity			
1003 vs	1007 vw	γ_{as} CH ₂ , β_{as} CH ₂ (overlapped)			
966 vs		γ_s CH ₂			
873 vw					
825 vw					

See footnote of Table 1 for elaboration of various symbols.

that γ_{as} Si-OC modes in (III) are higher by 15-20 cm⁻¹ than in the case of (II). This can be explained that Si-OCCCI skeletal stretching vibrations, mainly C-Cl stretching, is strongly mixed with the Si-OC mode whereas in the

case of (I), OC₂H₅ group frequencies do not interfere with Si-OC mode. For CH₂ stretching modes of OC₂H₄Cl in (III) two bands around 2960 cm⁻¹ were assigned. These bands are at lower frequency range than expected for

Table 3. Assignment of infrared frequencies of trivinyl chloroethoxy silane (III)

Infrared	Raman	Assignments	Infrared	Raman	Assignments
3061 m	3062 m,dp	$\nu_{as}CH_2$	1046 vs	1053 wd	$\nu_{as}CH_2$
			1014 s		$\beta_{as}CH_2$
2960 vs	2958 vs p	$\nu_{CH}, \nu_{CH_3}EtCl$			
2910 sh		ν_sCH_2	9655	973 vw dp	ν_sCH_2
2880 s	2872 vs,p	ν_sCH_2EtCl	839 s		$\beta_{as}CH_2EtCl$
2850 sh	2842 s,p	ν_sCH_2EtCl	773 vs		ν_sSiOC
1600	1602 m,p.	$\nu_{C=C}$			
1478 m	1484 vw				
1473 m	1463 w,dp	$\beta_sCH_2(EtCl)$	720		$\nu_{as}SiC_3$
1148 m	1434 w		668		
1427			666 m	670 m, dp	ν_{C-Cl}
1408	1413 wp	β_sCH_2	624	637 mp	ν_sSiC
1387 m	1384 vw	$\gamma_sCH_2(EtCl)$	548		γ_{CH}
1307 vs	1303 vw				
	1293 w,wdp	β_{CH}	310 s		$\beta_{CCCl}EtCl$
	1277		262 m	265 vw	δ_{OSiC}
1263 m	1260 vw dp	$\gamma_sCH_2(EtCl)$			
1203 s	1197 vw dp				
1127 sh	1134 w	$\nu_{as}SiOC$			
1100 vs		$\nu_{C-C}(EtCl)$			

See footnote of Table 1 for elaboration of various symbols.

$-OC_2H_4Cl$ group. These bands are effected by Fermi resonances with $2\delta CH_2$ levels. The C-H out of plane (γ_{CH}) vibration have been assigned at 542 cm^{-1} . The depolarized Raman bands exhibit minima at this frequency. Our assignment of this vibration at high frequency is contrary to that of Kalasinsky [16].

A two temperature (-70°) I.R. spectrum of (III) was recorded to observe the difference of eclipsed (IV) and gauche (V) forms. It was found none upto -70° which could be attributed to an increasing preference for a particular conformer, probably due to conformational complexity arising from the rotation about the C-Si, Si-O and O-C bonds.

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