

A STUDY OF $d_{\pi}-p_{\pi}$ INTERACTION IN ALKENYLSILANES

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Summary

The effects of $d_{\pi}-p_{\pi}$ interaction in alkenylsilane molecules containing different substituents at silicon have been studied by the method of ^{13}C NMR photoelectron spectroscopy and mass spectroscopy of negative ions.

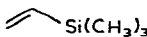
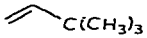
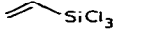
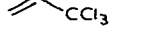
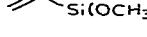
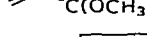
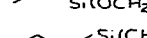




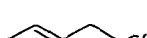



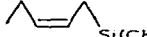

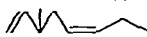

One of the interesting problems in the organic chemistry of silicon is the contribution of d -orbitals to the chemical bonds of silicon [1,2].

The effects of the $d_{\pi}-p_{\pi}$ interaction in alkenylsilanes containing different substituents at the silicon atoms, have been studied by ^{13}C NMR, photoelectron and negative ion mass spectroscopy.

The ^{13}C NMR spectra were recorded on a "Bruker" WH-90 (22.63 MHz) spectrometer with broad-band proton decoupling. When necessary, the spectra in a "monoresonant" regime were taken. The signal of the solvent CCl_4 was used as reference (96.0 ppm). The photoelectron spectra were recorded on a photoelectron spectrometer using (21.21 eV) He I ionization, made in our Institute. An electron energy analyzer of the Hughes-Rozhansky condenser type, and the analyzer with electron retardation by the retarding field (energy resolution 0.05 eV) were used. Mass spectra of negative ions were obtained as previously described [3]. The energy spread of the electrons was 0.3 eV at peak half height.

Table 1 contains the values of the chemical shifts (CS), and direct spin-spin coupling constants of some alkenylsilanes. The comparison of the vinylsilane ^{13}C NMR spectra with those of the hydrocarbon analogs ($\text{CH}_2=\text{CH}-\text{CX}_3$) shows that substitution of a carbon atom in the group CX_3 by a silicon atom leads to an increase in the shielding of the carbon α -atom, and to the decrease of shielding for the β -atom in the ethene radical. The chemical shifts of the carbon atom directly bonded to the silicon atom, C_{α} , are subjected to strong field displacements by about 9–12 ppm, while the chemical shifts of the C_{β} -atoms are displaced toward low field by about 21–23 ppm, compared with their isostructural hydrocarbon analogs. Values of the CS displacements are independent of

TABLE 1
 CHEMICAL SHIFTS OF ^{13}C NMR IN ALKENYLSILANES AND THEIR HYDROCARBON ANALOGS

Compound	δC_α (ppm)	δC_β (ppm)	δC_γ (ppm)	$J(C_\alpha-H)$ (Hz)	$J(C_\beta-H)$ (Hz)
	139.50	130.60		149	157
 ^a	149.0	109.0			
	131.0	138.70		152	163
	141.20	115.20		173	161
	127.70	135.60		142	157
 ^b	140.90	113.0			
	140.30	129.60		138	158
	24.66	134.1	112.5		
 ^c	48.86	136.10	116.50		
	18.45	126.50	120.75		
	43.3	128.60	125.10		
	23.20	126.50	122.50		
	50.10	128.80	126.90		
	18.90	125.0	126.80		
	43.30	127.0	131.50		
	18.60	124.40	129.0		
	43.30	126.40	133.0		
	18.50	125.40	125.90		
	43.30	127.70	129.90		

^a Data from ref. 4. ^b Calculated values. ^c Data from ref. 6.

the nature of X-atoms in the SiX_3 and CX_3 radicals, which is indicative of about the same force and direction of the induction effects caused by the X substituents, and which are transmitted through the carbon and silicon atoms to the carbon atoms of the ethene radical. The change in the value of chemical shifts of the C_α and C_β ethene atoms in the series $\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_3$, $\text{CH}_2=\text{CH}-\text{SiCl}_3$, and $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$ is similar to the change in CS of the same carbon atoms in their hydrocarbon analogs, which may be due to the induction

effects caused by SiX_3 and CX_3 groups and heteroatoms X.

In fact, in 3,3-dimethyl-1-butene at least two types of induction effects are present, resulting in a drift of valency electrons toward the double bond. It is known that the t-butyl group has a (+I)-effect [5]. Moreover, due to the hyperconjugation of the methyl group with the double-bond π -orbitals, the (+R)-effect is also present. As a result the terminal carbon atom, C_β , of the vinyl group is shielded more than the C_α atom.

In 3,3,3-trichloro-1-propene the chlorine atoms withdraw electrons, i.e. the (-I)-effect operates. On the other hand, the Cl atom also contains unshared pairs of electrons and therefore one can expect the (+R)-effect to act in the opposite direction. The combined effects cause a small increase in the electron density for C_α , and a decrease for C_β , compared with the electron densities at the corresponding atoms in 3,3-dimethyl-1-butene. In the silane series the same effects prevail, their force and direction being in fact coincident with the effects in the hydrocarbon analogs.

The comparison of ^{13}C NMR spectra of allylsilanes and their isostructural hydrocarbon analogs (whose spectra were either calculated from the scheme proposed in ref. 7, or taken from the literature) shows that replacement of a carbon atom by a silicon atom in the CR_3 group always results in a strong-field displacement of the carbon atoms by 24.6, 2.1, and 4.2 ppm for C_α , C_β and C_γ , respectively.

The changes observed in the chemical shifts of the alkenylsilanes, in comparison with those of their isostructural hydrocarbon analogs, and the fact that they are independent of the nature of the substituent X, are indicative of the main difference between Si and C atoms, i.e. the reduced electronegativity of Si, and the presence of vacant $3d$ -orbitals. If we admit a dative bond between the π -electrons of the vinyl group (in vinylsilanes) and one of the $3d$ -orbitals of the silicon atom, then the decrease in the C_β -atom shielding may arise [2] from the $d_\pi-p_\pi$ interaction reducing the π -electron density mainly on the C_β -atom. Owing to this interaction the nature of the substituent X does not practically affect the spin-spin constants, $J(\text{C}_\beta\text{-H})$. The strength of the $d_\pi-p_\pi$ dative bond is independent of the extent to which the other silicon $3d$ -orbitals are filled with the unshared electron pairs of the substituent X. The carbon C_α atom is always subjected to a strong field displacement due to the induction effect of the silicon atom, as a result of the lesser electronegativity of Si compared to that of C, and of the directivity toward the atom C_α . In the allylsilanes, only the +I-effect of the Si-atom operates, directed toward the alkenyl radical, whereas in vinylsilanes there is also an opposing $d_\pi-p_\pi$ interaction. As a result, the value of the CS displacement of the C_α -atom is smaller than in allylsilanes.

These conclusions are confirmed by the photoelectron spectroscopy data. Figure 1 shows the energy levels of the occupied molecular orbitals for trimethyltrimethoxy-, triethoxy-, and trichlorovinylsilanes and trimethylallylsilane. For two of these compounds the photoelectron spectra were obtained earlier. The spectra obtained in the present paper are similar to those reported [8]. A sharp decrease in the first ionization potential of trimethylallylsilane compared with that of trimethylvinylsilane, can be explained by a $\sigma-\pi$ -interaction between the double bond π -orbital and the σ -orbitals of the $\text{Si}-\text{C}\equiv$ group.

According to Weidner and Schweig [8] the ionization potentials of the

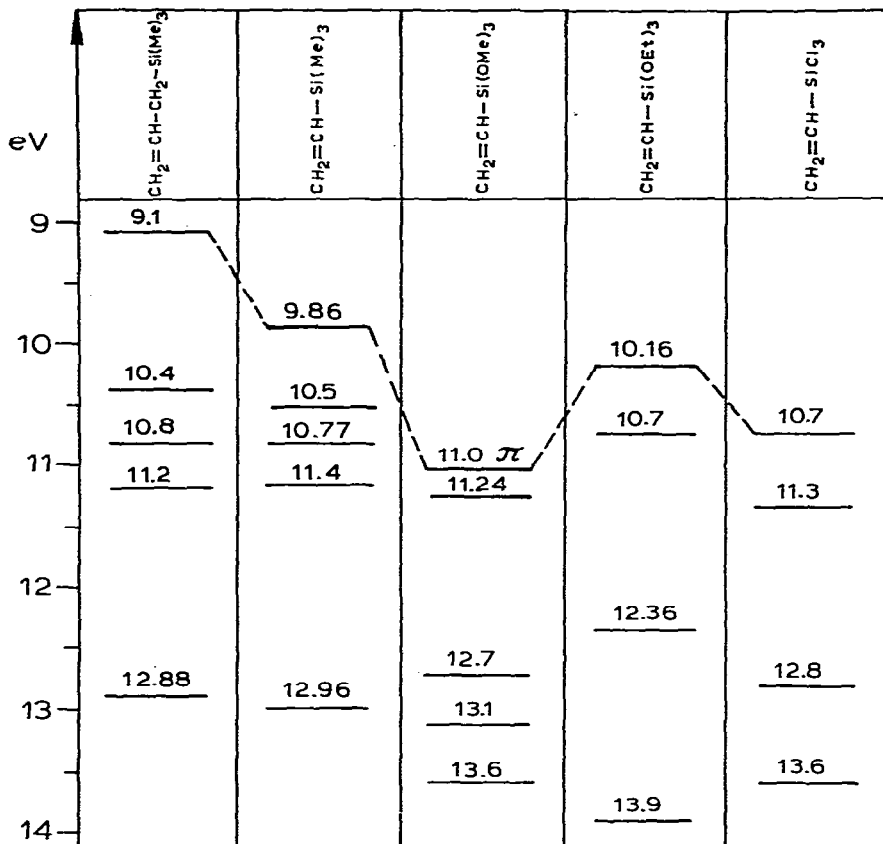


Fig. 1. Energy levels of the filled molecular orbitals in trimethylallylsilane and some vinylsilanes.

π -bond in vinyl silanes are always higher than the corresponding ionization potentials of hydrocarbon analogs. This fact is explained by a $d_{\pi}-p_{\pi}$ interaction in vinylsilanes, which increases the positive charge on the double bond.

From the data, it follows (see Fig. 1), that the nature of the substituent on the silicon atom determines the effective positive charge at the double bond. The positive charge increases in the order Me, OEt, Cl, OMe. Apparently, the σ -acceptor properties of the substituent facilitate the transfer of p_{π} -electrons to the silicon d -orbitals.

The same conclusion can be made from the negative ion mass spectrometry data for dissociative electron capture.

Table 2 lists the mass-spectra of some alkenylsilanes. The vinylsilane spectra contain the constituents ions, $(\text{CH}-\text{SiX}_3)^-$, which are formed as a result of the breakage of the double bond. But normally, the dissociative capture of electrons by alkenyl hydrocarbons does not occur [9-11]. Perhaps, the high stability of ions $(\text{CH}-\text{SiX}_3)^--\text{CH}=\text{SiX}_3$, (resulting from a "drift" of p_{π} -electrons to the vacant d -orbitals of the Si-atom under the action of the negative charge on the C-atom), allows the dissociation of the molecular negative ions to occur:

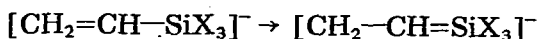


TABLE 2
 MASS SPECTRA OF NEGATIVE IONS OF THE DISSOCIATIVE ELECTRON CAPTURE BY $\text{CH}_2=\text{CH}-\text{SiX}_3$ AND $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}(\text{CH}_3)_3$ MOLECULES
 Relative intensities of mass lines are in % to the maximum; in brackets, the electron energy of the ion maximum yield, eV, ± 0.1 eV

Ions	$\text{CH}_2=\text{CH}-\text{Si}(\text{CH}_3)_3$	$\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$	$\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3$	$\text{CH}_2=\text{CH}-\text{SiCl}_3$	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}(\text{CH}_3)_3$
$(\text{M}-\text{H})^-$	100 (8.8)	1.9 (8.0)	1.0 (9.0)	—	100 (8.7)
$(\text{CH}-\text{SiX}_3)^-$	7.5 (3.7)	1.5 (6.7)	—	—	—
$(\text{M}-\text{X}_3)^-$	18.8 (8.6)	1.75 (7.8)	0.5 (9.5)	45.5 (7.6)	4.0 (8.9)
SiX_3^-	6.4 (9.0)	100 (6.3)	3.3 (6.8)	—	14.3 (6.7)
	25.0 (5.9)	—	—	—	—
	5.6 (6.0)	12.5 (7.2)	—	72.0 (6.1)	2.9 (8.0)
X^-	6.25 (7.2)	16.0 (6.3)	1.1 (9.5)	44.7 (4.1)	7.2 (5.6)
	—	100 (6.3)	1.3 (6.3)	100 (6.6)	17.0 (6.8)
CH_2^-	18.8 (9.2)	75.8 (8.4)	13.5 (12.0)	—	9.3 (7.0)
CH^-	23.8 (9.2)	35.0 (8.3)	53.0 (12.0)	—	4.3 (10.0)
O^-	—	12.5 (8.9)	87.0 (10.0)	—	2.2 (9.0)
	—	27.5 (5.0)	13.5 (7.0)	—	1.0 (4.0)
$(\text{M}-\text{C}_2\text{H}_5)^-$	—	—	100 (9.5)	—	—

Thus, from the ^{13}C NMR data it is possible to obtain the values of the relative charge distribution on C_α , C_β and C_γ atoms, attached to SiX_3 groups. But this method fails to give information about the value of the double bond charge. However, from photoelectron spectroscopy data we find that this depends on the substituents on silicon, and determines the extent of d_π - p_π coupling. Negative ion mass spectroscopy illustrates the role of the silicon d -orbitals in stabilizing the fragmentary ions and, is indirect evidence for the participation of Si-atom d -orbitals in the formation of the $\text{CH}=\text{Si}\leq$ bond.

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