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Corresponding Member of the Academy of Sciences of the USSR
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Abstract

Full Text

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INVESTIGATION OF THE VIBRATIONAL SPECTRA OF ETHYNYLSILANES

In recent years, researchers have been paying considerable attention to the study of monosubstituted silicon-acetylene compounds, which are of substantial theoretical and practical interest.

Fig. 1. Vibrational spectra of ethynylsilanes:
$(CH_3)_3SiC \equiv CH$ (*I*),
$(CH_3)_2Si(C \equiv CH)_2$ (*II*),
$(CH_3)Si(C \equiv CH)_3$ (*III*),
$Si(C \equiv CH)_4$ (*IV*),
$(CH_3)(CH{=}CH_2)Si(C \equiv CH)_2$ (*V*),
$(CH_3)_2SiHC \equiv CH$ (*VI*),
$(CH_3)(C_2H_5)SiHC \equiv CH$ (*VII*),
$(CH_3){-}SiH(C \equiv CH)_2$ (*VIII*).

In earlier studies on the properties of the acetylene bond in organosilicon compounds of the general structure $R_nSiC \equiv C - X$ (where R is CH_3 and C_2H_5, and X denotes various radicals) (^{1,8}), we showed that the vibration frequency of the $C \equiv C$ bond changes only slightly with different X. At the same time, the integral intensities depend substantially on the nature of the substituents, which indicates differences in the reactivity of silicon-acetylene compounds. The literature contains

Table 1

No.	Chemical compound	C C	C–H	Si–H	CH=CH$_2$	$J_{C\equiv C}$	$\frac{J_{C\equiv C}}{n}$
I	$(CH_3)_3SiC \equiv CH$ trimethylethynylsilane	2040 (s)	3276 (s)	–	–	141	141

No.	Chemical compound	C C	C–H	Si–H	CH=CH$_2$	$J_{C\equiv C}$	$\frac{J_{C\equiv C}}{n}$
II	$(CH_3)_2Si(C\equiv CH)_2$ dimethyldiethynylsilane	2046 (s)	3268 (s)	–	–	291.6	146
III	$(CH_3)Si(C\equiv CH)_3$ methyltriethynylsilane	2044 (s)	3270 (s)	–	–	425.7	142
IV	$Si(C\equiv CH)_4$ tetraethynylsilane	2050 (s)	3268 (s)	–	–	590	147
V	$(CH_3)(CH=CH_2)Si(C\equiv CH)_2$ methylvinyldiethynylsilane	2044 (s)	3276 (s)	–	3060 (m) 3020 (w) 1602 (w) 966 (m)	281.5	141
VI*	$(CH_3)_2SiHC\equiv CH$ dimethylethynylsilane	2046 (s)	3268 (m)	2126 (v.s.)	–	–	–
VII	$(CH_3)(C_2H_5)SiHC\equiv CH$ methylethylethynylsilane	2046 (s)	3270 (s)	2146 (s)	–	148	148
VIII	(CH_3)—$SiH(C\equiv CH)_2$ methyldiethynylsilane	2040 (s)	3268 (s)	2170 (s)	–	240.7	120

* The intensity could not be measured, since during recording the substance became colored.

data on vibrational spectra only for di- and trimethylethynylsilanes ([2],[3]). However, the intensity of the acetylene bond in such compounds had not been measured.

It seemed of interest to investigate the infrared absorption spectra and also to measure the intensities of the acetylene bonds of ethynylsilanes of the structure $R_nSi(C\equiv CH)_{4-n}$ ($n = 0 \div 3$, R—CH_3, C_2H_5, —$CH = CH_2$, —H), and thus to trace the change in the properties of the acetylene bond as ethynyl groups accumulate at the silicon atom.

The infrared spectra were obtained on an IKS-14 spectrometer in the regions 3300–1900 and 1700–660 cm^{-1} for compounds I–V, and in the region 3300–1900 cm^{-1} for the rest. The substances were recorded in the liquid state with an absorbing-layer thickness of 0.01 mm and in a solution of carbon tetrachloride ($C = 0.1$ mol/l; $d = 1.0$ mm).

The integral intensities of the acetylene bonds were measured from Raman spectra on an ISP-53 instrument. The reference was the carbon tetrachloride line with a vibrational frequency of 313 cm^{-1}, whose intensity was taken as 100 ([4]). The exciting mercury line was 4358 Å.

The principal absorption bands and their assignments are presented in Table 1 and in Fig. 1. The stretching vibration of the C C bond in all the compounds studied corresponds to an intense band with a maximum in the region 2040—2050 cm^{-1}.

Introduction of a silicon atom instead of a carbon atom in the α-position to the acetylene bond lowers the vibrational frequency of the latter by approximately 60—80 cm^{-1} (in monosubstituted alkynes $\nu_{C\equiv C}$ = 2140—2100 cm^{-1}). This is explained by a special type of interaction of the π-electrons of the acetylene bond with the vacant $3d$-orbitals of the silicon atom, leading to a withdrawal of electron-

of the bond cloud and to a change in its polarity, which causes a decrease in the vibrational frequency and an increase in intensity.

As was to be expected, the vibrational frequency of the C—H acetylenic bond is somewhat lower than in alkynes and lies in the region 3268-3280 cm^{-1}. The vibrational frequencies for compounds I and II are in full agreement with the literature data ([2,3]).

In compounds VI—VIII an increase in the frequency of the Si—H vibration is observed, from 2126 in VI to 2170 cm^{-1} in VIII. This is possibly connected with an increase in the electronegativity of the substituent groups at the silicon atom ([5]).

The vibrational frequencies of the vinyl group retain their usual values (3060, 3020, 1602, 966 cm^{-1}).

Yu. P. Egorov ([6,7]) showed that the intensity of double bonds for organosilicon compounds does not depend on the type of radicals at the silicon atom. As can be seen from the data in Table 1, the integral intensity of the acetylenic bond increases in proportion to the number of ethynyl groups at the silicon atom, remaining constant when calculated per one bond.

The characteristic nature of the frequency and intensity indicates the absence of interaction of the acetylenic bonds with one another and the presence of a strict characteristic nature for the whole group of bonds in the molecule.

The regularities obtained in the intensities make it possible to determine with confidence the number of acetylenic bonds in organosilicon compounds of the general structure $R_nSi(C\,CH)_{4-n}$ (where $n = 0 \div 3$). The structure of other organic radicals has no substantial influence on the frequency and intensity of the acetylenic bond.

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