THE α-EFFECT AND ROTATIONAL ISOMERISM IN SILYLMETHYL HALIDES $(CH_3)_2HSiCH_2Y$*

J.POLA, M.JAKOUBKOVÁ and V.CHVALOVSKÝ
Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

Received January 31st, 1977

Solvent and temperature dependence of the pattern of the ν(Si—H) absorption band and H-NMR spectra of the $(CH_3)_2HSiCH_2Y$ compounds with Y = Cl, Br and I are reported and the former discussed in terms of the α-effect and rotational isomerism in these compounds. Data on the α-effect in the α-carbofunctional compounds having hydrogens bonded to silicon have been compiled and hydrogen's response to the α-effect in these compounds is shown to be small.

An intramolecular interaction between a functional group and silicon termed the α-effect[1] was put forward[2,3] to illuminate unexpected properties of the α-carbofunctional organosilicon compounds (ref.[4,5] and refs included therein) and was treated by means of CNDO/2 calculation[6]. As to the compounds having hydrogen bonded to the silicon atom, many evidence of an unusual properties of the α-carbofunctional group or silicon atom in these compounds can be met in literature. First order rate constants for the acid-catalyzed hydrolysis of the RR′R″SiH compounds (the reaction slightly facilitated by electron withdrawal from the silicon atom) were found to correlate with Taft polar constant $\sum\sigma^*_{RR'R''}$ and substantial deviation from the correlation line (decreased reactivity) for the chloromethyldimethylsilane was ascribed to the direct interaction between filled *p* orbitals of the chlorine atom and vacant *d*-orbitals of the silicon atom[2]. IR hydrogen-bonding study of the $CH_3OCH_2MH_3$ compounds (M = C, Si) revealed that the organosilicon ether acts as a weaker proton acceptor than methylethylether, indicating thus, contrary to electronegativity prediction, H_3Si group to be less electron releasing than H_3C group[3]. The α-effect in chloromethyldimethylsilane was detected by an increase in the ^{35}Cl—NQR frequency of this compound with regard to its carbon analogue[1]. Finally, the decrease of the μ_{C-Y} bond dipole moment in the H_3SiCH_2Y compounds (Y = Cl, Br) was deduced from the dipole moment measurement of these compounds, and intramolecular interaction between halogen (especially chlorine) and the silicon atom was proposed to be responsible for it[7]. The last conclusion has support from the paper[4].

We dealt with an intramolecular interaction in chloromethylsilanes[4] and halogenomethylsilanes in general[5]. Recently published paper of Khorshev and coworkers[8] on the same phenomenon occurring in chloromethylsilanes having the hydrogen(s) bonded to the silicon forced us to report some our IR and NMR data on these compounds in order to show an erroneous conclusions on the α-effect made by the above authors.

---

* Part CLIII in the series Organosilicon Compounds; Part CLII: This Journal *42*, 2898 (1977).

DISCUSSION AND RESULTS

The rate controlling step of the acid-catalysed hydrolysis of organosilicon hydrides was assumed[9] to be nucleophilic attack of the water molecule to the complex formed by the electrophilic attack of hydronium ion to the organosilicon hydrides. The diminished reactivity of chloromethyldimethylsilane[8] has therefore to reflect chiefly the fact that electron density on silicon is higher than it would correspond to the I effect of the chloromethyl group. There are indications of lower electron density on a functional group in α-carbofunctional silylhydrides. The hydrogen-bonding studies demonstrate a decreased electron density on oxygen in $H_3SiCH_2OCH_3$ compound[3], and ^{35}Cl—NQR spectroscopy demonstrate a lower C—Cl σ-bond order in chloromethyldimethylsilane[1]. Recent ^{1}H-NMR data on the $H_3Si(CH_2)_n.$ $.OCH_3$ compounds ($n = 1-6$) revealed the remarkable constancy of the ^{13}C—H (OCH_3) coupling constants and $\tau(OCH_3)$ values in all these compounds and show thus the inability of the inductive effect to travel efficiently through the CH_2—O system[10]. (The methylene group was pointed out to absorb the changes in polar effect of the terminal molecular parts X and Y of the X_3MCH_2Y compounds with M = Si, Ge, Sn in general[5].) The greater magnitude of the ^{29}Si—H coupling constant for the compound with $n = 1$ compared to those with higher n indicates an increased s character of the Si orbital[10]. Mechanism proposed[6] for the α-effect ($n - \sigma + \sigma^*_{Si-C}$ orbital interaction) presumably results in some increase of the dipole moment of the Si—C bond, the fact being shown[4] not contradictive to the experimental dipole moment found for chloromethylsilane[7].

All the above data appear to be in harmony with the α-effect resulting in a decrease of electron density on a functional group, an increase of electron density on silicon and labilization of the Si—C bond. A question then arises how the hydrogen atoms on silicon experience the influence of the α-effect in the $H_nR_{3-n}SiCH_2Y$ compounds.

The proton chemical shift of H_3Si group in the H_3SiCH_2Y compounds (Y = = halogen) were reported to move with a variation of halogen in the opposite direction to that found for the proton chemical shift of the methylene group[11]. This empirical regularity is analogous to that reported for the α and β hydrogens of alkyl halides[12]. Proton chemical shifts of the methylene group in $(CH_3)_2HSiCH_2Y$ compounds bear a linear relationship to the Huggins electronegativity[13] of halogen, χ(Y), as is also observed with other silylmethylhalides[5], but both τH(Si) and τCH_3(Si) values are with these compounds for all Y unexpectadly constant (Table I). There is however difficult to put this "anomaly" into connection with the α-effect, since obscure situation is also met with alkyl halides[12] and deshielding effects of the halogens are not quite well understood at present[14,15]. (The methyl proton shits in the methyl derivatives and the methylene proton shifts in the ethyl derivatives are correlated well with substituent electronegativities, but the methyl proton shifts in the ethyl derivatives are not[16]. The trend of the dependance $\tau H(C—Y)$ *vs* electronegativity of Y for isopropyl halides is even reversed to that for methyl halides[12,16].) We therefore only point out here that substitution of hydrogen in the H_3SiCH_2Y compounds for CH_3 groups significantly changes the character of $\tau H(Si)$ *vs* $\chi(Y)$ plot equalizing all the $\tau H(Si)$ quantities regardless of the halogen nature.

Khorshev and coworkers[8] have recently attributed the IR doublet belonging to $\nu(Si—H)$ stretching vibration in $H_nSiR_{3-n}CH_2Cl$ compounds with $n = 1-3$ to the occurence of two types of molecules, the one without and the other with the "intramolecular coordination $Cl \rightarrow Si$ bond". The component of the bifurcated $\nu(Si—H)$ absorption band appearing at higher wavenumber was claimed to belong to the molecule in that the α-effect operates and the component appearing at lower wavenumber was considered to be due to the molecule free of the coordination bond. Furthermore, the concentration ratio of the both types of molecules was assesed from the components' intensities. Appearance of two or three bands for $\nu(Si—H)$ in di- or trihydrides is however inherent property of these compounds – it was convincingly shown to be the manifestation of the two types of stretching $\nu(Si-H)$ vibration-on-phase and out-of-phase one[17,18]. The double $\nu(Si—H)$ absorption with the compounds having only one hydrogen bonded to silicon was already earlier observed in our laboratory for some alkoxy(alkyl)silanes $R_n(RO)_{3-n}SiH$ with which the most pronounced phenomenon was ascertained with dialkoxysilanes[19]. Another recent findings that bifurcated $\nu(Si—H)$ band appears also in the spectra of halogenomethyldimethylsilanes was taken as evidence of at least two rotational isomers[20].

Hence, several $\nu(Si—H)$ absorption bands appear to be characteristic not only for chloromethylsilanes and not solely pertaining to the result of the α-effect. Temperature and solvent IR spectral measurements on the $H(CH_3)_2SiCH_2Y$ compounds with Y = Cl, Br, I carried out in this work were hoped to provide information on defined individual rotamers in these compounds and to shed more light on features determining the above $\nu(Si—H)$ band pattern. Our IR spectral measurements on the $H(CH_3)_2SiCH_2Y$ compounds in different solvents are in harmony with results reported for the $ClCH_2SiH_nR_{3-n}$ series by Khorshev and coworkers[8]. The pattern of the $\nu(Si—H)$ band in different solvents, as illustrated in Fig. 1, is strongly affected by solvent polarity. A single, almost symmetrical absorption band is observed in polar acetone (curve *6*), acetonitrile (curve *5*), and also in diethyl ether (curve *4*). Contrary to this finding, in nonpolar solvents as n-heptane (curve *2*), and tetrachloromethane (curve *3*), two bands appear symmetrically at both sides of the original $\nu(Si—H)$ wavenumber found in polar solvents. The doublet is also met in gases (Y = Cl, Br, I), while spectra measured in neat liquids provide one broader band, probable superposition of the aforementioned components. The separation of both maxima in n-heptane increases when going from chloride *via* bromide to iodide (Table I), and the intensity of the low-wavenumber component is in this solvent higher for all the halides, while the reverse situation is observed in CCl_4

and diethyl ether (Fig. 1). Based on our solvent measurement in the 3200–400 cm^{-1} region we consider the ν(Si—H) vibration the most sensitive to solvent changes of all spectral modes, since no other apparent changes were observed elsewhere in the IR spectra. The relative intensity decrease of the low-wavenumber component when going from n-heptane to CCl_4 or diethyl ether may reflect the shift in conformation equilibrium and temperature IR spectral measurements provide convincing evidence for it. The ν(Si—H) pattern showed itself, similarly as in solvent spectral measurements, to be the most sensitive to temperature variations of all other modes. As seen from Fig. 2 the intensity of the high-wavenumber component diminishes with decreasing temperature in n-heptane and tetrachloromethane as well. This shows the low-wavenumber component to belong to the rotamer with lesser energy content.

We can assume the presence of two most stable rotamers with $H(CH_3)_2SiCH_2Y$ compounds and a shift in their conformation equilibrium to be responsible for the observed variation of the ν(Si—H) pattern with temperature (Fig. 2), the low-wavenumber component being due to the more stable rotamer *I* and high-wavenumber component being due to the less stable rotamer *II*. The above observed IR spectra variation induced by the change of solvent enable us further to show the rotamer *I* to be less polar than rotamer *II*, because the intensity ratio of both the components

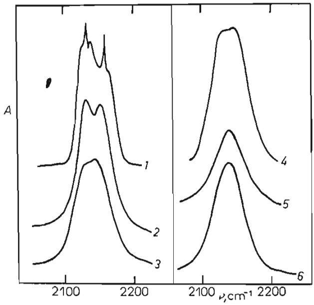


FIG. 1

IR Absorption Band of ν(Si—H) Stretching Vibration of Dimethyl (chloromethyl)silane in Gaseous State and Different Solvents

1 Gas; *2* n-heptane; *3* tetrachloromethane; *4* diethyl ether; *5* acetonitrile; *6* acetone.

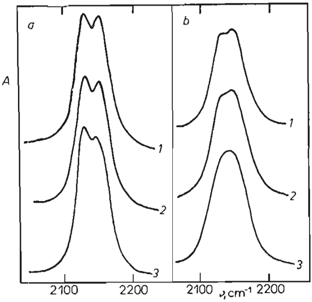
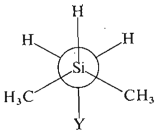


FIG. 2

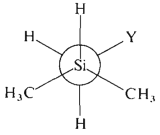
The ν(Si—H) Absorption Band of Dimethyl-(chloromethyl)-silane at Different Temperatures

a In n-heptane: *1* 60°C; *2* 30°C; *3* −90°C; *b* in tetrachloromethane: *1* 90°C; *2* 30°C; *3* −25°C.

changes in favour of the low-wavenumber one when going from n-heptane to CCl_4 or diethyl ether.



I



II

We are aware of possibility of an intermolecular solute-solute interaction inferred for the H_3SiCH_2Y (Y = Cl, Br, I) compounds on the grounds of the ^{1}H-NMR dilution shift data[11]. The ν(Si—H) pattern with the $(CH_3)_2HSiCH_2Y$ compounds in neat liquids appears to be consistent with such type of interactions as well, since only solute–solute interactions in neat liquids could have brought about the coalescence of both the ν(Si—H) band components. On the grounds of the concentration of $H(CH_3)_2SiCH_2Y$ compounds used (10^{-1}M), and of the dependence of the ν(Si—H) pattern on the solvent polarity we are however inclined to assume solute–solvent interaction as being dominant with the solutions of the $(CH_3)_2HSiCH_2Y$ compounds in polar solvents like acetone and acetonitrile. We can therefore presume that the ν(Si—H) pattern with the halogenomethylsilanes can be accounted for by the rotational isomerism, and the less polar rotamer with antiperiplanar arrangement of Si—H and C—Cl bonds is of lower energy content, *i.e.* more stable.

The $n - \sigma + \sigma^*_{Si-C}$ molecular interaction was recommended as explanation of the α-effect in the H_3SiCH_2X compounds (X = F, OH, NH_2), but relevance of the other possible modes like $n - \sigma + \sigma^*_{Si-H}$ importance of those would differ for rotamers *I* and *II* was put forward too[6]. This arises the question whether one rotamer could possess more suitable conditions for the α-effect operation than the other. The interaction of polar molecules like acetone, CH_3CN and alike with organosilicon compounds without proton-donating groups are generally assumed to be realized chiefly through participation of the silicon atom. Such intermolecular interaction can be suggested also with $(CH_3)_2HSiCH_2Y$ compounds, since intermolecular interactions including their halogen seem to be of less importance, and so do the interactions including solely negatively charged hydrogen of Si—H bond. Assuming then the rotamer *I* as being less polar (even if the α-effect operates only in rotamer *I*, it can hardly overweight the influence of total molecular polarity by mutual arrangement of polar Si—H and C—Cl bonds), solute–solute interactions in neat liquids or solute solvent interactions in polar solvents were above shown to decrease its concentration, what may apparently reflect its lower electron density on silicon compared to that in rotamer *II*. This would imply the α-effect operation in conformer *II*,

TABLE I

The ν(Si—H) Wavenumbers, in cm^{-1}, and ^1H-Chemical Shifts, τ(H) in ppm units for the $(CH_3)_2$ $.HSiCH_2Y$ Compounds

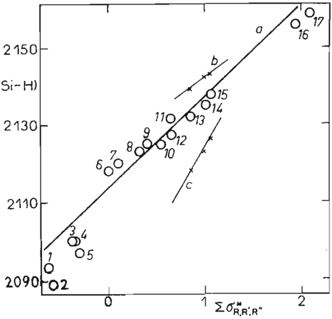
Y	$\tau(H)^a$			ν(Si—H)		
	H(Si)	CH_3	CH_2	n-heptane	CCl_4	CH_3CN
Cl	5·91	9·78	7·19	2 127 2 147	2 126 2 143	2 137
Br	5·88	9·76	7·51	2 124 2 148	2 123 2 142	2 131
I	5·89	9·78	7·98	2 120 2 147	2 118 2 139	2 130

[a] 15% (v/v) CCl_4 solutions.

FIG. 3

Plot of the ν(Si—H) Value *vs* $\sum\sigma^*_{R,R',R''}$ Constant for RR'R"SiH Compounds

The numbering of the points pertaining to line *a* corresponds to the following data from references[27–30] (number, RR'R"Si, ν(Si—H) in cm^{-1}, $\sum\sigma^*_{RR'R''}$): *1*, $(s\text{-}C_4H_9)_3Si$, 2093, −0·63; *2*, $(i\text{-}C_3H_7)_3Si$, 2088, −0·57; *3* $(i\text{-}C_4H_9)_3Si$, 2100, −0·38; *4*, $(n\text{-}C_3H_7)_3Si$, 2100, −0·35; *5*, $(C_2H_5)_3Si$, 2097, −0·30; *6*, $(CH_3)_3Si$, 2118, 0; *7*, $(i\text{-}C_4H_9)(CH_2{=}{=}CHCH_2)_2Si$, 2120, 0·10; *8*, $(CH_3)_2.(CF_3CH_2CH_2)Si$, 2123, 0·32; *9*, $CH_3.(CH_2{=}CHCH_2)_2Si$, 2125, 0·40; *10*, $C_2H_5.(CF_3CH_2CH_2)_2Si$, 2125, 0·54; *11*, $CH_3.(CF_3CH_2CH_2)_2Si$, 2132, 0·64; *12*, $(C_6H_5.CH_2)_3Si$, 2127, 0·65; *13*, $(CH_3)_2(JCH_2)Si$, 2132, 0·85; *14*, $(CH_3)_2(BrCH_2)Si$, 2135, 1·00; *15*, $(CH_3)_2(ClCH_2\ )Si$, 2138, 1·05; *16*, $(CH_3)_2(Cl_2CH)Si$, 2156, 1·94; *17*, $CH_3(ClCH_2)_2Si$, 2159, 2·10. Asterisks relate to the ν(Si—H) band components with the $H(CH_3)_2SiCH_2Y$ compounds where Y = = Cl, Br and I, and the dependence of the ν(Si—H) of high-vawenumber and low-vave-number component on the halogen variation is depicted by line *b* and *c* respectively.



that manifests itself by the highwavenumber component of the ν(Si—H) absorption band.

The magnitude of the ν(Si—H) stretching frequency might be a good indicator of a role of the α-effect in both the rotamers, since its very high sensitivity[21] to the polar effects of substituents bonded to silicon and its sensitive response to back bonding between some substituents and silicon is well documented[22–25]. However, the ν(Si—H) *vs* $\sum^{*}_{RR'R''}$ plot for the organosilicon hydrides RR'R"SiH having both R, R', R" groups operating solely through their inductive effect (alkyl and $CF_3CH_2.CH_2$ groups) and CH_2X groups, X substituent of those is claimed to be engaged in the α-effect, seems to be the same for both series of the compounds[26]. This situation is seen with more data on Fig. 3, in which the ν(Si—H) wavenumbers observed for both the components of bifurcated ν(Si—H) band with $(CH_3)_2HSiCH_2Y$ compounds (Table I) are marked by asterisks. Low-wavenumber component was claimed by Khorshev[8] to belong to a "molecule with Cl →Si coordination bond". However, we have demonstrated that if the α-effect is responsible for the double ν(Si—H) absorption it has to be of greater importance in rotamer *II* which manifests itself by the high-wavenumber component and the ν(Si—H) of that are seen on Fig. 3 not to deviate downward from the correlation line.

We can therefore conclude that the pattern of the ν(Si—H) absorption band is chiefly determined by the conformation heterogeneity, *i.e.*, by different dipole–dipole and steric interactions in neighbourhood of the Si—H bond in both the conformers. In a view of greater sensitivity of the ν(Si—H) value of rotamer *II* (low-wavenumber component) to halogen variation (Fig. 3, Table I) the effect of dipole–dipole interaction appears to dominate. The α-effect convincingly demonstrated to play a significant role in determining of the properties of the α-carbofunctional organosilicon compounds with hydrogens bonded to silicon turns out to influence the nature of the Si—H bond unimportantly.

EXPERIMENTAL

Halogenomethyldimethylsilanes $(CH_3)_2HSiCH_2Y$ with Y = Cl, Br, I were prepared according to the described procedures[31–33]. Their physical constants agreed with those reported in literature. The purity of all the compounds was checked by gas-liquid chromatography.

Infrared spectra of halogenomethyldimethylsilanes were recorded in gas, neat liquids and different solvents with a double beam Zeiss, Model UR-20 spectrometer. Concentration of the compounds in CCl_4, CS_2, heptane, CH_3CN, diethylether, and acetone was about 10^{-1}M. The frequency scale of the instrument was calibrated in the usual way. The IR spectra of the solutions of the compounds in n-heptane and CCl_4 were measured at different temperatures(+90°C to −90°C) in temperature controled cell with AgCl windows produced by RIIC. Thickness of the cell was 0·01 cm. ^{1}H-NMR spectra were recorded for the CCl_4 solutions of the compounds (15% v/v) on a modified Tesla BS 467 spectrometer (60 MHz), using cyclohexane as internal reference compound. Chemical shifts were determined with an accuracy of ±0·01 ppm.

We thank Mr M. Pultr for NMR measurement.

REFERENCES

1. Voronkov M. G., Feshin V. P., Mironov V. F., Mikhailants S. A., Gar T. K.: Zh. Obshch. Khim. *41*, 2211 (1971).
2. Steward O. W., Pierce O. R.: J. Amer. Chem. Soc. *83*, 4932 (1961).
3. Wang J. T., Van Dyke C. H.: Inorg. Chem. *6*, 1741 (1967).
4. Pola J., Chvalovský V.: This Journal, in press.
5. Pola J., Chvalovský V.: This Journal, in press.
6. Ponec R., Chvalovský V.: This Journal *40*, 2309 (1975).
7. Bellama J. M., McDiarmid A. G.: J. Organometal. Chem. *24*, 91 (1970).
8. Khorshev S. Ya., Egorochkin A. N., Sevastyanova E. I., Ostasheva N. S., Kuzmin O. V.: Zh. Obshch. Khim. *46*, 1801 (1976).
9. Eaborn C.: *Organosilicon Compounds*, p. 204. Butterworths, London 1960.
10. Bellama J. M., Gerchman L. L.: Inorg. Chem. *14*, 1618 (1975).
11. Bellama J. M., McDiarmid A. G.: J. Organometal. Chem. *18*, 275 (1969).
12. Cavanaugh J. R., Dailey B. P.: J. Chem. Phys. *34*, 1099 (1961).
13. Huggins M. L.: J. Amer. Chem. Soc. *75*, 4123 (1953).
14. Tribble M. T., Traynham J. G. in the book: *Advances in Linear Free Energy Relationship* (N. B. Chapman, J. Shorter, Eds). Plenum Press, London 1972.
15. Hamer G. K., Reynolds W. F.: Can. J. Chem. *46*, 3813 (1968).
16. Bothner-By A. A., Naar-Colin C.: J. Amer. Chem. Soc. *80*, 1728 (1958).
17. Ohno K., Murata H.: Bull. Chem. Soc. Jap. *45*, 3333 (1972).
18. Hayashi M., Ohno K., Murata H.: Bull. Chem. Soc. Jap. *46*, 797 (1973).
19. Jakoubková M.: Unpublished results.
20. Reich P., Koehler P., Licht K., Kriegsmann H.: Z. Chem. *14*, 413 (1974).
21. Kovalev I. P.: Dokl. Akad. Nauk SSSR *134*, 559 (1960).
22. Thompson H. W.: Spectrochim. Acta *16*, 238 (1960).
23. Kriegsman H., Kessler G., Reich P.: Z. Chem. *1*, 346 (1961).
24. Attridge C. J.: J. Organometal. Chem. *13*, 259 (1968).
25. Egorochkin A. N., Khorshev S. Ya., Vyazankin N. S., Chernysheva T. I., Kuzmin O. V.: Izv. Akad. Nauk SSSR *1971*, 544.
26. Mileshkevich V. P., Novikova N. F., Karkin A. V.: Org. Reactiv. *8*, 1093 (1971).
27. Kessler G., Kriegsmann H.: Z. Anorg. Allg. Chem. *342*, 63 (1966).
28. Ponomarenko V. A., Egorov Yu. P.: Izv. Akad. Nauk SSSR, Ser. Khim. *1960*, 1133.
29. Shevchenko I. V., Kovalev I. F., Arbuzova V. A., Voronkov M. G., Khudobin Yu. P.: Dokl. Akad. Nauk SSSR *192*, 842 (1970).
30. Kriegsmann H., Reich P., Schott G., Werner H.: Z. Anorg. Allg. Chem. *343*, 101 (1966).
31. Kaesz H. D., Stone F. G. A.: J. Chem. Soc. *1957*, 1433.
32. Schott G., Werner H.: Z. Anorg. Allg. Chem. *331*, 51, (1964).
33. Sommer L. H., Bennett O. F.: J. Amer. Chem. Soc. *81*, 251 (1959).

Translated by the author (J. P.).