

## ORGANOSILICON COMPOUNDS. LXXXII.\*

## MOLECULAR COMPLEXES OF PHENYLMETHYLCHLOROSILANES AND VINYLMETHYLCHLOROSILANES WITH BROMINE AND IODINE\*\*

I. VÉLE, V. VAJSAROVÁ and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, Prague-Suchdol*

Received February 8th, 1971

Molecular complexes of silicon compounds of the types  $C_6H_5(CH_3)_{3-n}SiCl_n$ ,  $CH_2=CH.(CH_3)_{3-n}SiCl_n$ , and  $C_6H_5CH_2(CH_3)_{3-n}SiCl_n$  with iodine and bromine have been studied by UV spectra and dipole moment measurements. These complexes can affect reactivity of the components. Their equilibrium constants increase with increasing number of methyl groups attached to the silicon atom. Phenylmethylchlorosilanes form stronger complexes with bromine than with iodine.

Anomalies observed in the course of our studies of various reactions of organosilicon compounds with iodine and bromine<sup>1</sup> compelled us to examine the ability of phenylmethylchlorosilanes and vinylmethylchlorosilanes to form complexes with iodine or bromine. As proved already with a series of methylchlorosilanes<sup>1</sup>, the formation of complexes would not be appreciably affected by methylchlorosilyl groups. It can be therefore expected that a complex bond will be formed between the aromatic or olefinic part of the molecule and the halogen. A great number of charge-transfer complexes of this type have already been reported in literature. Their formation and properties have been thoroughly studied, especially in the case of carbon compounds<sup>2</sup>. An important work devoted to the formation of complexes of silyl-, alkyl- and silylalkyl-substituted benzenes with tetracyanoethylene is that of Bock and Alt<sup>3</sup> dealing with the role of a ( $p \rightarrow d$ ) $\pi$  nature of the silicon-phenyl bond.

## EXPERIMENTAL

Iodine, bromine and solvents were from the same sources as in the previous work<sup>1</sup>. The preparation and purity of the phenylmethylchlorosilanes<sup>4</sup> and benzylmethylchlorosilanes<sup>5</sup> studied were already reported. Vinyltrichlorosilane and vinylmethyldichlorosilane were purified by distilla-

\* Part LXXXI: This Journal 36, 4111 (1971).

\*\* A summary of this work was presented at IV. Intern. Conf. on Organometallic Chemistry, Bristol 1969; see M. I. Bruce and F. G. A. Stone: *Progress in Organometal. Chem.*, D 10. Chemical Society, London, 1969.

tion, as described in the previous work<sup>1</sup>. Vinyltrimethylchlorosilane was prepared by a reaction of dimethyldichlorosilane with vinylmagnesium chloride<sup>6</sup>, vinyltrimethylsilane was obtained by methylation of vinyltrichlorosilane<sup>7</sup> with methylmagnesium chloride. Both compounds were purified by fractional distillation and their purity was checked by gas chromatography. The systems were measured under the same conditions as in the previous work<sup>1</sup>. The same method as in the previous work<sup>1</sup> was used in measurements of dielectric constants.

## RESULTS

Phenylchlorosilanes dissolved in cyclohexane have characteristic spectrum of benzene and its derivatives. At wavelengths above 280 nm the absorption of the phenyl group is small enough to allow detection of new complex absorption bands, even though both bands sometimes partly overlap.

In the spectra of ternary systems phenylmethylchlorosilanes-iodine-cyclohexane the absorption bands corresponding to the complexes of the silanes with iodine were observed for the three members of this series, phenyltrimethylsilane, phenyldimethylchlorosilane, and phenylmethyldichlorosilane (Table I). No absorption band which could be assigned to the complex has been found, however, in the spectrum of phenyltrichlorosilane. Equilibrium constants of these complexes, calculated by Henessi-Hildebrand method<sup>8</sup>, are given in Table I. From the Table it follows that the donor ability of a silane increases with increasing number of the methyl groups in its molecule, which reflects in increasing value of the equilibrium constant of the complex. At the same time the absorption band maximum shifts to longer wavelengths. The

TABLE I

Molar Absorptivities  $\epsilon_{\max}$  and Equilibrium Constants  $K_c$  of Complexes of Phenylmethylchlorosilanes with Iodine and Bromine in Cyclohexane and Tetrachloromethane

System	Quantity	$C_6H_5(CH_3)_3Si$	$C_6H_5(CH_3)_2SiCl$	$C_6H_5(CH_3)SiCl_2$	$C_6H_5SiCl_3$
Silane + I <sub>2</sub> + + cyclohexane	$\lambda_{\max}$	300	290	287.5	—
	$\epsilon_{\max}$	6 570	8 620	7 710	—
	$K_c$	0.52 ± 0.02	0.33 ± 0.04	0.24 ± 0.01	—
Silane + I <sub>2</sub> + + CCl <sub>4</sub>	$\lambda_{\max}$	300	290	287.5	—
	$\epsilon_{\max}$	3 920	5 450	1 330	—
	$K_c$	0.76 ± 0.03	0.22 ± 0.04	0.14 ± 0.01	—
Silane + Br <sub>2</sub> + + CCl <sub>4</sub>	$\lambda_{\max}$	290	290	290	290
	$\epsilon_{\max}$	1 000	1 080	3 390	2 770
	$K_c$	1.85 ± 0.22	0.32 ± 0.03	0.45 ± 0.03	0.25 ± 0.05

blue shift of the visible iodine absorption band is not great, in the spectra of first three members of the series the iodine band is shifted to 520 nm. This fact is in harmony with assumption that phenylmethylchlorosilanes, similarly as all methyl-substituted benzenes such as toluene and xylene, due to their relatively weak donor ability, form predominantly complexes of collision type. The ground state of collision complexes is only very little stabilized by the dative form of the complex bond. Ionic character of the acceptor iodine is therefore developed only to a small extent, and so the visible iodine absorption band is only little blue-shifted<sup>9</sup>.

From dielectric measurements of this series of compounds and from the equilibrium constants determined spectrally we calculated dipole moments for the following complexes: phenyltrimethylsilane  $\mu_{\text{complex}} = 8.2 \text{ D}$ ; phenyldimethylchlorosilane  $\mu_{\text{complex}} = 6.6 \text{ D}$ ; phenylmethyldichlorosilane  $\mu_{\text{complex}} = 1.5 \text{ D}$ . These values further support the assumption that the donor ability of phenyl-substituted silanes increases with increasing number of the methyl groups and decreasing number of chloro-substituents.

The results of the measurements of the ternary systems phenylmethylchlorosilanes-iodine-tetrachloromethane can be interpreted in a similar manner (Table I). Dependence of equilibrium constants of the complexes on the donor ability of the silanes is the same as in the systems discussed in the preceding paragraphs. A decrease in the intensity of the complex bands can be explained<sup>10</sup> by an increased participation of collision form of the complex in the structure of the complex. The visible iodine absorption band is shifted to 515 nm.

In the ternary systems phenylmethylchlorosilanes-bromine- $\text{CCl}_4$  the complexes are formed by all members of this series. The complex absorption band lies at 290 nm. The equilibrium constants of the formation of the complexes increase with increasing donor ability of the silanes, the only exception being an anomalous value of the equilibrium constant for phenyldimethylchlorosilane.

Systems in which vinylmethylchlorosilanes were used as donors were studied only qualitatively, since a quantitative analysis was made impossible by a change of the spectrum with time. The measurements were carried out at  $-10 \pm 0.2^\circ\text{C}$ . This temperature was chosen with the aim to suppress bromination of these compounds and also with respect to a low boiling point of the first member of the series-vinyltrimethylsilane.

In the spectra of solutions of iodine in vinyltrimethylsilane the visible iodine absorption band is markedly shifted (430 nm). After some time, the intensity of the band increases and the absorption band maximum shifts to 440 nm. In the ternary system ( $\text{CCl}_4$  as the solvent) the visible iodine absorption band lies at 505 nm and its intensity is higher than in the binary system; its position is time dependent and shifts to shorter wavelength region.

In the spectrum of the ternary system with vinyldimethylchlorosilane as a donor, the visible iodine band maximum lies at 515 nm. However, after the period of 30

minutes the band is shifted to 510 nm, a new absorption band with maximum at 395 nm being formed. Similar results were also obtained with vinylmethylchlorosilane. Only with the binary and ternary systems of vinyltrichlorosilane we observed a new absorption band at 282.5 nm, from which data necessary for the calculation of the equilibrium constant of the complex ( $K_c = 0.39 \pm 0.01$ ) and of molar absorptivity ( $\epsilon_{\max} 4951 \text{ mol}^{-1} \text{ cm}^{-1}$ ) have been obtained.

The instrument used prevented us to study this series in detail. From the shifts of the visible iodine absorption maximum it can be concluded that also here the formation of a complex, probably of several different forms, takes place. The presence of more than one form might account for time-dependence of the spectrum. It seems that for first two members of the series the initial form of the complex, the formation of which is probably kinetically controlled, is slowly transformed into another form, the formation of which is controlled thermodynamically. This form is more stable than the first one and its formation gives rise to a new absorption band occurring at 450 nm for vinyltrimethylsilane and at 395 nm for vinyldimethylchlorosilane.

The formation of complexes of the series of benzylmethylchlorosilanes with iodine as the acceptor was studied in their ternary solutions in cyclohexane or tetrachloromethane. When using the donor in concentration differing from that of the acceptor by two to three orders of magnitude, the shoulder of a new band appeared in the spectrum, indicating the formation of the complex. The complex band maximum could be determined only with difficulty, since the overlap with the absorption band of benzylmethylchlorosilane was very great. The same observation has already been made by Bock and Alt<sup>3</sup>. This overlap makes a quantitative analysis of the spectrum impossible. For this reason the separation of both bands reported<sup>3</sup> for the complexes of benzylmethylchlorosilanes has not been attempted. The visible iodine absorption band appears at 510 nm in the case of benzyltrimethylsilane and is shifted to 525 nm in the case of benzyltrichlorosilane, depending on the number of the methyl groups.

## DISCUSSION

From the results of spectral measurements of the series of phenylmethylchlorosilanes it follows that the tendency to form complexes is in this series greater than in the series of methylchlorosilanes<sup>1</sup>, the complexes are however less stable with iodine than with bromine. This unexpected result is difficult to explain, since in the interaction of  $\pi$ -electron system of the benzene ring with an acceptor more favourable conditions for maximum overlap of the donor with the acceptor orbitals are formed in the case of iodine molecule.

On comparing the equilibrium constants obtained for the complexes of this series with iodine in both nonpolar solvents used with the analogous data reported for benzene derivatives<sup>11</sup> we found that  $K_c$  for the complex of phenyltrimethylsilane is very close to  $K_c$  for mesitylene. Analogously, phenyldimethylchlorosilane can be

compared with *o*- or *p*-xylene, and phenyldimethylchlorosilane with benzene. These results show that the silyl groups affect the electron density on the benzene ring mainly by their comparatively strong positive inductive effect, increasing thus its donor ability; at the same time they do not directly take part in the formation of the complex. This is in harmony with the assumed structure of the complexes of iodine with benzene derivatives, based on the measurements of carbon compounds<sup>12</sup>.

Of the carbon analogues of phenylmethylchlorosilanes we measured *tert*-butylbenzene. The equilibrium constant for the complex with iodine was found to be  $0.40 \pm 0.01$ . This value is lower than that obtained for the complex of phenyltrimethylsilane with iodine ( $K_c = 0.76 \pm 0.03$ ) which further demonstrates a comparatively great effect of the silyl groups on the formation of the complexes. These complexes may also affect reactivity of the compounds studied.

From the results obtained for the series of vinylmethylchlorosilanes it is obvious that these compounds are able to form complexes with halogens, even though a more detailed study of their formation is impeded by experimental difficulties. It can be assumed, however, that the complexes of these compounds are comparatively strong and can affect reactivity of the components. Similar conclusions can be drawn from the measurements of the series of benzylmethylchlorosilanes. In this case, too, a quantitative analysis is impossible.

Our results support conclusions of Bock and Alt<sup>3</sup> that the complex bands of silyl-substituted benzenes occur at shorter wavelengths than the corresponding bands of their carbon analogues. Silyl groups affect the benzene ring by inductive polarization  $+I_{SiR_3} > +I_{CR_3}$ . The back interaction  $Si \leftarrow C$  of the benzene ring with silicon  $3d$ -orbitals could not be studied in our systems because of difficult separation of the complex bands and their partial overlap with the  ${}^1L_0$  band of the benzene nucleus.

#### REFERENCES

1. Véle I., Vaisarová V., Hetflejš J., Chvalovský V.: This Journal 36, 4111 (1971).
2. Saksena B. D., Kagaris R. E.: J. Chem. Phys. 19, 994 (1951).
3. Bock H., Alt H.: J. Am. Chem. Soc. 92, 1569 (1970).
4. Lepeška B., Chvalovský V.: This Journal 34, 3556 (1969).
5. Včelák J., Bažant V., Chvalovský V.: This Journal 35, 136 (1970).
6. Koutková J., Chvalovský V.: This Journal, in press.
7. Cudlín J., Chvalovský V.: This Journal 27, 1658 (1962).
8. Henessi H. A., Hildebrand J. H.: J. Am. Chem. Soc. 70, 2832 (1948).
9. Slivkin M. A.: Nature 198, 1301 (1963).
10. Orgel L. E., Mulliken R. S.: J. Am. Chem. Soc. 87, 167 (1965).
11. McGlynn S. P., Roggus I. D.: J. Am. Chem. Soc. 80, 5096 (1958).
12. Mulliken R. S.: Rec. Trav. Chim. 75, 845 (1956).

Translated by J. Hetflejš.