

## ORGANOSILICON COMPOUNDS. LXXXI.\*

MOLECULAR COMPLEXES OF METHYLCHLOROSILANES  
AND METHYLMETHOXYSILANES WITH IODINE AND BROMINE

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In the course of our studies on halogenation of some organosilicon compounds we have observed a number of anomalies. Electrophilic bromination of phenylhalogenosilanes catalyzed with iron tribromide gave higher yields of *meta*-derivatives<sup>1</sup>, compared with analogous electrophilic chlorination of these compounds<sup>2,3</sup>. The proportion of the *meta*-derivatives was, however, markedly reduced, and that both in chlorination and bromination, when iodine was employed as the catalyst: in a series of the silanes  $C_6H_5Si(CH_3)_{3-n}X_n$  this difference increased with increasing  $n$  from 0 to 3<sup>2,3</sup>. Similar differences in the proportion of *meta*-derivatives has also been observed between the  $FeCl_3$ - and  $I_2$ - catalyzed chlorination of phenylmethylchlorogermanes<sup>4</sup>. In this connection it is of interest to mention a markedly reduced rate of the addition of bromine to 1-heptane in the presence of vinyltrichlorosilane<sup>5</sup>. Another anomalous phenomenon has been encountered during bromination of the Si—H bond of the hydrides  $R_{3-n}X_nSiH$ : while with  $X = Cl$  or  $Br$  the reaction was first order in bromine, the second<sup>6</sup>-order reaction in bromine was observed when  $X$  was an alkoxy group.

All these anomalies may be accounted for by assuming that organosilicon compounds of the type  $Y_4-nSiZ_n$  (where  $Y$  is vinyl or phenyl group, and  $Z$  is halogen or alkoxy group) are able to form charge-transfer complexes with molecular bromine or iodine. With the aim to ascertain whether apart from vinyl or phenyl groups present in the molecules of these compounds, also the rest of the molecule, the silyl group  $-SiZ_n$ , can take part in the formation of these complexes, we decided to study the formation of such molecular complexes between methylchlorosilanes (and for comparison also germanium and carbon analogues thereof) or alkoxy silanes and bromine or iodine.

At present much attention is being paid<sup>7</sup> to theory of charge-transfer complexes in all fields of chemistry. Yet, only a few cryoscopic and refractometric measurements<sup>8-10</sup> has been made with organosilicon and -germanium compounds. In the present study we have chosen more convenient spectroscopic methods<sup>1</sup> and dipole moment measurements. The equilibrium constants of formation of molecular complexes can relatively easily be determined with the aid of Benesi-Hildebrand equation<sup>12</sup> or of some of their modified versions<sup>13</sup>. From the magnitude of equilibrium constants some conclusions can be drawn on the predominant form of the complex<sup>14</sup>.

## EXPERIMENTAL

## Chemicals Used

Iodine (analytical purity grade) was resublimed prior to its application. Bromine (analytical purity grade, Polskie Odczynniki Chem., Gliwice, Poland) was used without further purification. Cyclohexane (analytical purity grade) was three times hydrogenated, dried by boiling it with

phosphorus pentoxide, and then distilled over a 45–50 TP glass distillation column filled with metal wire rings. Its purity was checked spectroscopically (100% transmittance at 220 nm). Tetrachloromethane (analytical purity grade), tert-butyl chloride, and 2,2-dichloropropane were dried over phosphorus pentoxide and then distilled through the same column as in the preceding case (100% transmittance from 270 nm). All the solvents used were stored over a Nalsit 4A molecular sieve<sup>4</sup>.

Silicon tetrachloride, methyltrichlorosilane, dimethyldichlorosilane (chemical purity grade, VCHZ-Synthesia, Kolín) were distilled before use through a 12 TP distillation column filled with Dixon rings made from a copper gauze. Trimethylchlorosilane and tetramethylsilane were prepared by methylation<sup>15</sup> of dimethyldichlorosilane with methyl chloride in the presence of aluminium powder at 350°C.

Trimethylchlorogermane, dimethyldichlorogermane, and methyltrichlorogermane were obtained by the direct synthesis described elsewhere<sup>16</sup>. Their purity was checked by determination of chlorine content, elemental analysis and by gas chromatography.

Trimethylmethoxysilane and dimethyldimethoxysilane were prepared by esterification of the appropriate chlorosilanes by stoichiometric amount of anhydrous methanol in the presence of equimolar amounts of dry pyridine<sup>17</sup>. Methyltrimethoxysilane was obtained in a similar fashion, with the use of quinoline. The products were freed from trace amounts of pyridine (quinoline) hydrochloride by multiple distillation. Tetramethoxysilane was prepared from tetra-methylsilane in the usual manner<sup>8</sup>. The product was freed from minute amounts of hydrogen chloride by distillation in the presence of anhydrous calcium carbonate. The purity of the compounds was checked by gas chromatography. Boiling points and refractive indices of the prepared methoxysilanes agreed well with literature data.

#### Procedure

Dipole moments were determined by measuring concentration dependences of dielectric constants and densities of the silanes. Dielectric constants were measured on an instrument designed after Le Fevre<sup>19</sup> and operating on the basis of resonance method. Dipole moments were calculated according to Halverstadt and Kumler<sup>20</sup>.

Ultraviolet spectra were measured on Hilger-Gilford spectrophotometer at the temperature  $25 \pm 0.05^\circ\text{C}$ , except measurements with tetramethylsilane which were carried out at  $-10 \pm 0.2^\circ\text{C}$ .

Two facts were considered as evidence for the formation of charge-transfer complexes: non-zero value of the equilibrium constant of the formation of the complex,  $K_c$ , and finite value of molar absorptivity of the complex absorption band  $E_{\text{max}}$ . The methylchlorosilanes and methylchlorogermanes were measured both in the binary system chlorosilane(germane)iodine (or bromine) and in the ternary systems with the use of tetrachloromethane, cyclohexane, or acetonitrile as solvents. Because of ready hydrolysability of these substances, all manipulations were carried out in a dry box filled with nitrogen.

Dielectric measurements were made with the ternary systems chlorosilanes(germanes)iodine (the acceptor) and cyclohexane (the solvent). Dielectric constants and densities (determined with a Sprengel–Ostwald pycnometer with accuracy of  $5 \cdot 10^{-5}$  g/mol) were measured at  $25 \pm 0.05^\circ\text{C}$ .

#### RESULTS AND DISCUSSION

Methylchlorosilanes, except dimethyldichlorosilane, do not show significant absorption at wavelengths above 240 nm (the molar absorptivities are smaller than 0.05 l/mol cm). The spectrum of dimethyldichlorosilane is anomalous, since it exhibits five absorption bands at 238, 242.5,

250, 255 and 260 nm. Threshold of transmittance in the spectrum of tetramethylsilane is markedly shifted to longer wavelengths, compared to other members of this series. The spectra of these compounds in different solvents have similar features. In the binary system chlorosilane-iodine we have observed no change in the spectrum with  $\text{SiCl}_4$ ,  $\text{CH}_3\text{SiCl}_3$ , and  $(\text{CH}_3)_2\text{SiCl}_2$ . Contrarily, a new absorption band at 278.5 nm or 272.5 nm appeared in the spectrum of  $(\text{CH}_3)_2\text{SiCl}_2$ ,  $\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$ , respectively. As expected, the maximum of visible iodine absorption band shifted to shorter wavelengths as the number of methyl groups increased (blue shift). Tetramethylsilane is exceptional in its behaviour, since its presence does not effect the position of the iodine band (Table I).

Starting from the results obtained for the binary system, we were able to prove the formation of the complex in the ternary system dimethyldichlorosilane-iodine-carbon tetrachloride. The equilibrium constant was found to be  $0.25 \pm 0.01$ . The position of the maximum of the complex band was 287.5 nm. Similarly, in the ternary system with cyclohexane and iodine, the complex was detected only with dimethyldichlorosilane. The position of the absorption band maximum was identical with the preceding case, the equilibrium constant amounted to  $0.39 \pm 0.02$ .

The ternary systems methylchlorosilane-iodine-acetonitrile have not been studied in detail since we found that iodine and acetonitrile form a complex which exhibits three new absorption bands at 265, 287.5, and 365 nm; the maximum of the visible iodine absorption band is shifted to 460 nm. In the ternary system with dimethyldichlorosilane, the band at 265 nm disappears, while the intensity of the two remaining band increases. In the system dimethyldichlorosilane-bromine-carbon tetrachloride, the complex band lies at 282.5 nm; the equilibrium constant was found to be  $0.20 \pm 0.01$ . Changes in dipole moments of the ternary solutions methylchlorosilane-iodine-cyclohexane, relative to solutions of methylchlorosilanes in cyclohexane, are very small. Only by using the equilibrium constant of the complex of dimethyldichlorosilane with iodine found spectroscopically, we were able to determine<sup>21</sup> the dipole moment of this complex  $\mu = 1.70$  D.

With the methylchlorogermans we first measured the spectra of the binary systems with iodine as the acceptor. We found that the ability to form complex increases with increasing number of the methyl groups. In difference to dimethyldichlorosilane, dimethyldichlorogermane did not

TABLE I

Dependence of Molar Absorptivities  $E_{\max}$  and Maxima of Visible Iodine Absorption Band  $\lambda_{\max}$  (nm) on Structure of Compounds  $(\text{CH}_3)_{4-n}\text{MCl}_n$  ( $M = \text{Si, Ge}$ )

Compound	$(\text{CH}_3)_{4-n}\text{MCl}_n-\text{I}_2$		$(\text{CH}_3)_{4-n}\text{MCl}_n-\text{I}_2-\text{CCl}_4$	
	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$
$\text{SiCl}_4$	518	820	518	800
$\text{CH}_3\text{SiCl}_3$	510	745	515	825
$(\text{CH}_3)_2\text{SiCl}_2$	505	720	515	850
$(\text{CH}_3)_3\text{SiCl}$	500	520	510	—
$(\text{CH}_3)_4\text{Si}$	525	490	—	—
$\text{CH}_3\text{GeCl}_3$	510	800	515	850
$(\text{CH}_3)_2\text{GeCl}_2$	505	740	510	850
$(\text{CH}_3)_3\text{GeCl}$	490	670	495	750

behave anomalously. On the other hand, in the spectrum of trimethylchlorogermane there appeared two absorption bands, one at 292.5 nm and the other at 380 nm. The maxima of visible iodine absorption bands were shifted to shorter wavelengths (Table I). In the ternary system with tetrachloromethane all the maxima either disappeared or overlapped with the absorption band of germane to the extent which prevented to quantitatively analyse the spectrum. The maxima of visible iodine absorption bands were shifted to longer wavelengths and their molar absorptivities increased over those for the binary system (Table I).

In the spectra of the binary mixtures of the carbon analogues (tert-butyl chloride and 2,2-dichloropropane) with iodine, no new absorption bands have been observed. The visible iodine band maximum was shifted to 515 nm.

The methylmethoxysilanes measured *in substantia* showed negligible absorption above 240 nm. The absorption markedly increased, however, towards the shorter wavelength region. The spectra of the binary systems alkoxyisilane-iodine, measured with water as blank, exhibited two absorption bands, the visible iodine absorption band (515 nm) with the molar absorptivity 2400 l/mol cm and the ultraviolet band, which was identical with that observed in the spectra of the alkoxyisilanes measured *in substantia*. We were not able to find any band which could be ascribed to the charge-transfer complex. The measurements with the use of the corresponding alkoxyisilane as the reference solution were made impossible by strong absorption of the alkoxyisilanes in the 220–240 nm region.

For this reason we used the ternary systems alkoxyisilane-iodine-cyclohexane. The spectra were measured relative to the solution of alkoxyisilane (of the same concentration as that used in the ternary system) in cyclohexane. The measurements were carried out with three ternary systems, the concentration of iodine always being  $5 \cdot 10^{-4}$  mol/l and that of alkoxyisilane being 0.5, 1.0, and 2.0 mol/l, respectively. The spectra of all the ternary systems showed similar features: a) only two absorption bands appeared, b) the maximum of the visible iodine absorption band (515 nm) was shifted to shorter wavelengths in the ternary system, when compared with cyclohexane (525 nm). Its position did not depend significantly on the structure of alkoxyisilane. The ultraviolet absorption band (238 nm) which was shifted by 3 nm relative to the band in cyclohexane (235 nm), behaved similarly, c) the absorption in the maxima of the two bands did not depend on the concentration of alkoxyisilane in the ternary system. In this case, too, we were not able to detect any new absorption band or a shoulder on the long-wavelength side of the ultraviolet absorption band which would indicate the formation of the charge-transfer complex. We do not believe this results can be considered as evidence against the formation of such a complex, since it cannot be excluded that the charge-transfer band is located in the region of the contact charge-transfer band of iodine with the solvent<sup>22</sup>. A somewhat increased absorptivity in the maximum of this band in the ternary system over that in cyclohexane seems to support this assumption.

#### REFERENCES

1. Včelák J., Chvalovský V.: This Journal, in press.
2. Lepeška B., Chvalovský V.: This Journal 34, 3553 (1969).
3. Lepeška B., Bažant V., Chvalovský V.: J. Organometal. Chem. 23, 41 (1970).
4. Lepeška B., Chvalovský V.: This Journal 35, 261 (1970).
5. Koutková J., Chvalovský V.: This Journal, in press.
6. Hetflejš J.: Unpublished results.
7. Mulliken R. S.: J. Chem. Phys. 7, 14 (1939).
8. Dejč A., Voronkov M. G.: *International Symposium on Organosilicon Chemistry, Prague 1965*, Scientific Communications, p. 252.

9. Dejm A., Voronkov N. G.: Latvijas SSR Zinatna Akad. Nauk, Chim. Sec. 1966, 39.
10. Voronkov M. G., Dejm A.: Latvijas SSR Zinatna Akad. Nauk, Chim. Sec. 1965, 689.
11. Mulliken R. S.: J. Am. Chem. Soc. 74, 811 (1952).
12. Benesi H. A., Hildebrand J. H.: J. Am. Chem. Soc. 70, 2832 (1948).
13. Rose M. J., Drago R. S.: J. Am. Chem. Soc. 81, 6138 (1959).
14. Orgel L. E., Mulliken R. S.: J. Am. Chem. Soc. 79, 4838 (1957).
15. Hurd D. T.: J. Am. Chem. Soc. 67, 1545 (1945).
16. Lepeška N., Chvalovsky V.: This Journal 35, 261 (1970).
17. Kantor W. S.: J. Am. Chem. Soc. 75, 2712 (1953).
18. Sumrell G., Hane G. E.: J. Am. Chem. Soc. 78, 5573 (1956).
19. LeFevre R. J. W., Russell P.: Trans. Faraday Soc. 43, 374 (1947).
20. Halverstadt I. F., Kummeler W. P.: J. Am. Chem. Soc. 64, 3988 (1942).
21. Kortüm G., Walz H.: Z. Elektrochem. 57, 73 (1953).
22. Julien L. M., Bennett W. E., Perodu W. B.: J. Am. Chem. Soc. 91, 6915 (1969).

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#### NOTE CONCERNING THE KINETICS OF HYDROLYSIS OF SCHIFF BASES OBTAINED FROM SALICYLALDEHYDES

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I have read with interest the paper of Hoffmann and coworkers on the kinetic of hydrolysis of substituted salicylideneanilines<sup>1</sup>, and I would like to make the following comments.

In a previous paper<sup>2</sup> we have reported the results of a study on the hydrolysis of hydroxy and methoxy derivatives of N-benzylidene-2-aminopropane. The experimental rate constants for the *ortho* and *para* hydroxy derivatives have been shown to be a function of true rate and equilibrium constants (Eq. (1)) corresponding to the mechanism given in Scheme 1.

$$k_{\text{obs}} = \frac{k_1 k_4 [\text{H}^+] + k_2 k_4 \cdot 10^{14} + k_3 k_4 K_1 [\text{OH}^-]}{\{K_1 + [\text{H}^+] + K_1 K_2 / [\text{H}^+]\} \{k_{-1} [\text{H}^+] + k_{-2} + k_{-3} [\text{OH}^-] + k_4\}} \quad (1)$$

Thus, one has to take into account the existence of a tautomeric equilibrium with an equilibrium constant  $K_T$ . The relations (2) between the different equilibrium constants are:

$$\begin{aligned} K_T &= [\text{S}]/[\text{T}], \quad K_{\text{SH}^+} = [\text{S}][\text{H}^+]/[\text{SH}^+], \quad K_{\text{TH}^+} = [\text{T}][\text{H}^+]/[\text{SH}^+], \\ K_T &= K_{\text{SH}^+}/K_{\text{TH}^+} \end{aligned} \quad (2)$$