ORGANOSILICON COMPOUNDS. CVI.*

CT SPECTRA AS A MEANS OF THE STUDY OF THE ORIGIN OF INTRAMOLECULAR INTERACTIONS IN ALLYLSILANES

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CT spectra of the allylsilanes $X_3SiCH_2CH{=}CH_2$ ($X = Cl, C_2H_5O, H, CH_3$) and of some carbon analogues with tetracyanoethylene as an acceptor were measured in dichloromethane. The changes in the wavenumbers of charge-transfer bands, ν_{CT}, due to changes in substitution on silicon are in harmony with the assumption of hyperconjugative interaction of the silicon with the β unsaturated group. This is confirmed also by the results of CNDO/2 calculations of allylsilane and by simple correlation diagrams based on them. On their basis as well as on the basis of arguments of perturbation theory the acceptor properties of silicon are explained by the presence of low lying $\sigma^*(CH_2{-}Si)$ antibonding orbitals rather than 3*d* orbitals. This assumption comports with the following sequence of the electron-accepting strength of the β-silicon atom: $SiCl_3 > SiH_3 > Si(OC_2H_5)_3 > Si(CH_3)_3$.

The essence of intramolecular interactions in α-and β-carbofunctional silicon derivatives is at present the subject of rapidly growing interest. This was stimulated by Pitt's suggestion[1] of hyperconjugation as an alternative mechanism to $(p \rightarrow d)\,\pi$ interactions in organosilicon compounds, when the earlier suggestion by Nesmeyanov[2] of $\sigma - \sigma$ conjugation had remained unnoticed. A deeper insight to this problem was introduced by quantum chemistry, which with recent development and availability of the methods involving all valence electrons can give if not yet quite quantitative, so certainly correct qualitative description of physical reality. Thus Schweig by the use of CNDO/2 method has shown for allyltrimethylsilane that the inclusion of 3*d* silicon orbitals does not explain the order and magnitude of orbital energies represented by experimental ionisation potentials obtained by photoelectron spectroscopy. Similarly, Pitt[4] has proved by means of CNDO/2 method the acceptor properties of the SiH_3 group in phenylsilane without inclusion of 3*d* silicon orbitals. On the basis of these and other quantum chemical data the effort has recently been made to detect hyperconjugation effect by the use of various experimental techniques, such as ^{29}Si and ^{13}C NMR spectroscopy or basicity measurements by IR spectrometry[5-8]. None of them is, however, comparable in elegancy and unambiguousness to photoelectron spectroscopy, since the quantities measured (chemical shifts δ or $\Delta\nu_{OH}$) do not depend only on the respective electron densities. This is clearly demonstrated, for instance, by Jones[9] who in correlating ^{13}C NMR chemical shifts of monosubstituted benzenes with CNDO/2 total charges on the respective carbon atoms had to make also allowance for magnetic anisotropy of some substituents. This sets limits to the discussion of chemical shifts in terms of the concept of hypercon-

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jugation as expressed by limiting structures of valence bond theory. For these reasons photoelectron spectroscopy, or the spectroscopy of charge-transfer complexes, providing directly the quantities relating to orbital energies (or only HOMO, *cf.* Koopmans[10]) seem to be the most suitable methods. Excelent correlations of the values of the excitation energies ν_{CT} of charge-transfer bands with available ionisation potentials[11,12] can serve as a proof of adequacy of this method. The character of charge-transfer complexes under study as π-complexes is also proved by this correlation. Furthermore, the shifts in the values of orbital energies can also be estimated with the aid of Hoffman's concepts[13] of interaction of orbitals "through space" and "through bond", which becomes extraordinarily useful tool for fast orientation, without sometimes time-consuming and expensive calculations.

The aim of this work was to interpret with the aid of the above assumptions the CT spectra of a series of allylsilanes differing in substituents on silicon. A series of analogous vinylsilanes was chosen for comparison purposes. Due to the fact that in the vinylsilane series we deal with the interaction of the π orbital directly with $\sigma^*(Si—X)$ antibonding orbital whose energy is more sensitive to variations of X than the energy of the $\sigma^*(X_3Si—CH_2)$ orbital, corresponding changes in charge-transfer spectra of the vinylsilanes should be more pronounced. This is indicated *e.g.* by the values of ν_{CT} of the excitation energies of charge-transfer bands of substituted phenylsilanes[14,15].

EXPERIMENTAL

Model compounds. All the compounds studied were prepared by literature procedures. Table I presents therefore only their characteristic constants with corresponding references to their synthesis. The exception was allylsilane which was prepared by a modified procedure which will be described later. The purity of all the compounds was checked by gas chromatography. In no case the compounds contained more than 0·5% of impurities. Allylsilane was prepared by reduction of allyltrichlorosilane with $NaAlH_2(OCH_2CH_2OCH_3)_2$ in benzene. Owing to sufficiently different boiling points allylsilane was distilled directly from the reaction mixture and, after cooling in a distillation head, was collected in a flask cooled with dry ice. As checked by gas chromatography the product did not contain benzene, not even in trace amounts. 2,2-Dimethyl-4-pentene (*purum*) and 2,2-dimethyl-3-butene (*purum*), supplied by Fluka, were purified by fractional distillation. Tetracyanoethylene (TCNE) (*purum*, Fluka A.G.) was used without further purification. Dichloromethane (analytical purity grade, Lachema Works, Brno) was purified by repeated washing with sodium carbonate aqueous solution, dried over anhydrous calcium chloride and distilled through 1 m-column filled with ceramic rings. The fraction boiling 39—39·5°C was collected and stored in a dark flask over Nalsit 4A molecular sieve.

Charge-transfer spectra of the studied compounds with tetracyanoethylene in dichloromethane were recorded on Specord spectrometer (Zeiss, Jena) in the 15000—35000 cm^{-1} region. The quartz cells were 1 cm thick. The measurements were carried out with respect to the pure solvent. The concentration of the donors was about 0·1M, that of tetracyanoethylene was varied from 0·001 to 0·1M in dependence on the donor used. It was proved that the position of charge-transfer bands does not depend on the acceptor concentration. Because of relatively weak donor ability of the allylsilanes, the accuracy of the reading of CT band maximum was about ± 200 cm^{-1}, in the case of allyltrichlorosilane even worse, since the charge-transfer band lies close to the region

TABLE I

Characteristic Constants of and Literature Data on Compounds Studied

Compound	B.p., °C/Torr found (lit.)	n_D^{20} found (lit.)
$CH_2{=}CH{-}CH_2SiCl_3$	117 (114–115/743[19])	1·4445 (1·4460[19])
$CH_2{=}CH{-}CH_2SiH_3$	18 (16·9[23])	— (1·4050[23])[a]
$CH_2{=}CH{-}CH_2Si(OEt)_3$	177 (100/50[22])	1·4059 (1·4073[22])
$CH_2{=}CH{-}CH_2{-}SiMe_3$	82 (82·8–8·3[20])	1·4087 (1·4070[20])
$CH_2{=}CH{-}(CH_2)_2SiMe_3$	112 (110·5/752[21])	1·4127 (1·4149[21])
$CH_2{=}CH{-}CH_2CMe_3$	—	1·4810 —
$CH_2{=}CH{-}CMe_3$	41 (41·2[24])	1·3750 (1·3760[24])

TABLE II

Wavenumbers of Charge-Transfer Bands of Studied Compounds with TCNE in Dichloromethane

Compound	$10^{-3} \cdot \nu$, cm^{-1}	Compound	$10^{-3} \cdot \nu$, cm^{-1}
$CH_2{=}CH{-}CH_2SiCl_3$	30·3	$CH_2{=}CH{-}CH_2SiMe_3$	24·1
$CH_2{=}CH{-}CH_2{-}Si(OEt)_3$	26·6[a]	$CH_2{=}CH{-}CH_2CMe_3$	28·5[a]
$CH_2{=}CH{-}CH_2{-}SiH_3$	27·5	$CH_2{=}CH{-}(CH_2)_2SiMe_3$	27·0[a]
$CH_2{=}CH{-}CMe_3$	29·7		

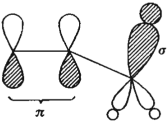
[a] Shoulder.

of the proper absorption of tetracyanoethylene. The decrease of the concentration of TCNE does not result in separation of the absorption bands, since in such a case the band corresponding to charge-transfer complex is of low intensity. Of the series of analogous substituted vinyl derivatives, due to the low intensity of the charge-transfer band, we were able to determine only the position of CT band in the case of 2,2-dimethyl-3-butene. Already with vinyltrimethylsilane we found that the CT band lies in the region of the proper absorption of TCNE. For this reason no attempts have been made to record the spectra of the other vinylsilanes of the type $CH_2{=}CH{-}SiX_3$ ($X = Cl$, C_2H_5O). The wavenumbers of CT bands of all the compounds studied are given in Table II.

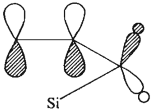
DISCUSSION

In the first study ascribing the so-called β-effect to hyperconjugation, Schweig[3] prefers for allyltrimethylsilane on the basis of CNDO/2 calculations conformation *I*.

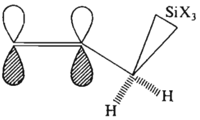
Similar conclusion has recently been reached also by Bock[12] who employed CNDO/2 method with Del Bene and Jaffé parametrisation. Both authors find the frontier orbital (HOMO) of the π–σ form *A* for conformation *I*, and of the form *B* for conformation *II*. Owing to the greater polarisability of Si—C bonds than of C—H bonds, one can expect the greater changes in HOMO energy with substitution at silicon (which, of course, affects the Si—CH_2 bond) for conformation *I* than for conformation *II*, quite in harmony with the results of similar measurements of the CT spectra of a series of silacyclopentenes[14] where, due to rigid skeleton, the compounds are solely in conformation *II*. Starting from the form of these CNDO/2 wave functions and from Hoffmann's concept of interaction of orbitals "through space", we may attempt to estimate changes in HOMO energies for derivatives differing in substitution at silicon on the basis of simple orbital diagrams (Scheme 1).



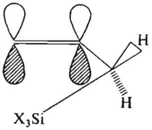
A



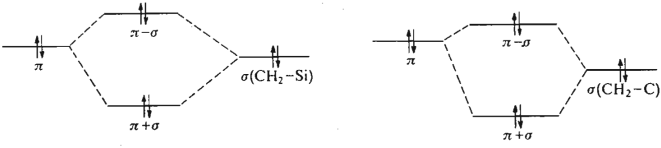
B



I

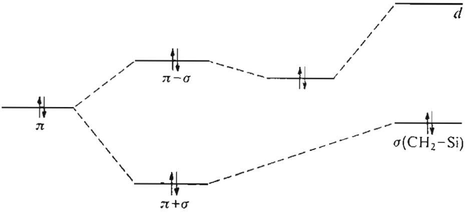


II



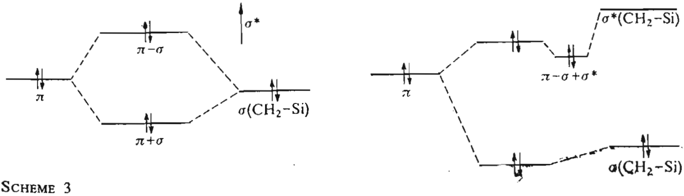
Scheme 1

With respect to greater electropositivity of silicon, the energy of $\sigma(\text{Si—CH}_2)$ would be certainly higher than that of $\sigma(\text{C—CH}_2)$ in respective carbon analogue, which will make the interaction with π-orbital easier and will result in a decrease of ionisation potential. This is the case. The value of ν_{CT} of allyltrimethylsilane is lower than that of 2,2-dimethyl-4-pentene. It should be mentioned that in the case of closed shell systems the above-mentioned interaction of orbitals does not lead to the changes of total charge distribution. The decreased ionisation potential of allylsilane, relative to allyltrimethylsilane, is ascribed by Bock to the interaction with *d*-orbital. (Scheme 2)



SCHEME 2

On the basis of perturbation theory the decrease in HOMO energy with increasing electronegativity of the groups attached to silicon can be accounted for by the participation of $\sigma^*(\text{CH}_2\text{—Si})$ orbital rather than of *d* orbital in the following way. The *d* orbital can stabilise itself only by participation in the bond, however, a considerable difference between its energy and the energy of HOMO operates against such a stabilisation. It is true that the interaction leading to HOMO of the π–σ type increases the energy of HOMO and makes then the interaction with *d* orbital more favourable. If such model were correct, the greatest decrease caused by $(d$–$\pi)$ interaction should be observed with strongest donors. By contrast, ν_{CT} and hence also ionisation potential of allyltrifluorosilane decrease even below the level of the carbon standard, 2,2-dimethyl-4-pentene.



SCHEME 3

The explanation can be found by considering σ^* antibonding orbitals. With increasing electronegativity of the groups at silicon the *d*-orbital will be increasingly contracted, which enhances its bonding ability without change in its energy. Contrarily, the energy of both $\sigma(CH_2—Si)$ and $\sigma^*(CH_2—Si)$ will decrease, the result being a great improvement of the possibility of the interaction due to the decrease of the energy difference $[HOMO - \sigma^*(CH_2\text{-}Si)]$. With the aid of orbital diagrams this can be depicted as follows (Scheme 3). As the electronegativity of X increases, the interaction decreasing ionisation potential becomes gradually less important (decrease of $\sigma(CH_2—Si)$), while the $\sigma^*–\pi$ interaction leading to increase of ionisation potential becomes more important. Whether and when the energy of HOMO will decrease below the level of the carbon standard depends on relative magnitudes of the energy of the π-component, $\sigma(CH_2—Si)$ and $\sigma^*(CH_2—Si)$ and on corresponding β integrals.

In the series of the substituted allylsilanes under study the order of ν_{CT} is following: $SiCl_3 > C(CH_3)_3 > SiH_3 > Si(OC_2H_5)_3 > Si(CH_3)_3$. The $SiCl_3$ group only acts hence as an acceptor. In analogous series of benzylsilanes even the SiF_3 group is still the donor[15]. The role of the decrease of the energy of antibonding orbitals and of their strong interaction with occupied orbitals, speaking for the necessity of the description of ground states of molecules by means of configuration interaction with inclusion of doubly excited configurations was convincingly shown *e.g.* by Epiotis[16] on the example of the violation of the validity of well-known Woodward–Hoffmann rules for (2 + 2) cycloadditions, *e.g.* in decreasing stereospecificity of *trans*-addition of halogens to ethylene with increasing electronegativity of the halogen. Also Schweig's recent studies on the photoelectron spectra[17,18] of allyl and benzyl halogenides, establishing the decrease of ionisation potentials in the order I > Br > Cl > F, exclude the participation of *d* orbitals and are, on the contrary, quite consistent with the suggested explanation. The importance of σ–π-conjugation in the allyl derivatives of Group IVb elements reveals also the results reported by Bach[25], obtained by extended Hückel method. Similarly to CNDO/2 methods, also here the frontier orbital was found to be of the π–σ type. In addition, the author studied also the effect of protonation of the β-carbon which leads to strong decrease in population in the $CH_2—M$ bond. The cation of this type is therefore stabilized vertically[26,27], which is the evidence of hyperconjugation and, at the same time, excludes any intramolecular coordination. The same conclusion can also be drawn from comparison of excitation energies (see Table II) of ν_{CT} of allyl- and γ-butenyltrimethylsilane.

The calculations proving the importance of σ^* orbitals on the properties of ground states of such compounds are at present under preparation in this laboratory.

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