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THEORY AND APPLICATION OF PHOTOELECTRON SPECTROSCOPY

V*. THE NATURE OF BONDING IN VINYL- AND ALLYLSILANES: THE EFFECTS OF σ–π (HYPERCONJUGATION) AND p_π–d_π CONJUGATION IN THESE COMPOUNDS

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SUMMARY

The photoelectron spectra of vinylsilane (II), trimethylvinylsilane (IV), and trimethylallylsilane (VI) have been recorded along with those of the corresponding carbon compounds propene (I), 3,3-dimethyl-1-butene (III), and 4,4-dimethyl-1-pentene (V). Comparison reveals a close parallel between the highest occupied MO's in the silicon compounds and those in the carbon compounds. The electronic structure of both series of compounds is discussed in terms of bond energies (C–H, C–C, Si–H, Si–C bonds), of hyperconjugative interaction of these bonds with the ethylene π MO, and of p_π–d_π conjugation between the d_π AO's on the silicon atom and the adjacent π MO. The importance of p_π–d_π bonding in vinylsilanes (involving the Si–C bonds) is clearly established from valence electron calculations (MINDO/1 and CNDO/2).

RESULTS AND DISCUSSION

Fig. 1 shows the HeI (584 Å) photoelectron spectra of molecules (I) to (VI), measured on a Perkin–Elmer PS16 instrument. Fig. 2 presents relevant parts of these spectra on an expanded scale. In Fig. 3 the measured vertical ionization potentials (*IP*) and the relative band intensities of both series of compounds are compared. In Fig. 4 are shown the calculated HOMO energies of the carbon and corresponding silicon compounds; in the latter case the energies have been calculated with (*spd*) and without (*sp*) inclusion of *d* AO's on the silicon atom.

We first consider the spectra of the carbon compounds. The spectrum of propene (I) shows five peaks on the low ionization energy side. Both MINDO/1[1] and CNDO/2[2] calculations yield a similar pattern for the highest occupied MO's: $\pi_1, \sigma_1, \sigma_2, \sigma_3$ and π_2. The HOMO (one node between the ethylene π-MO and the

(*continued on p.* 264)

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[*] For Part IV see ref. 3.

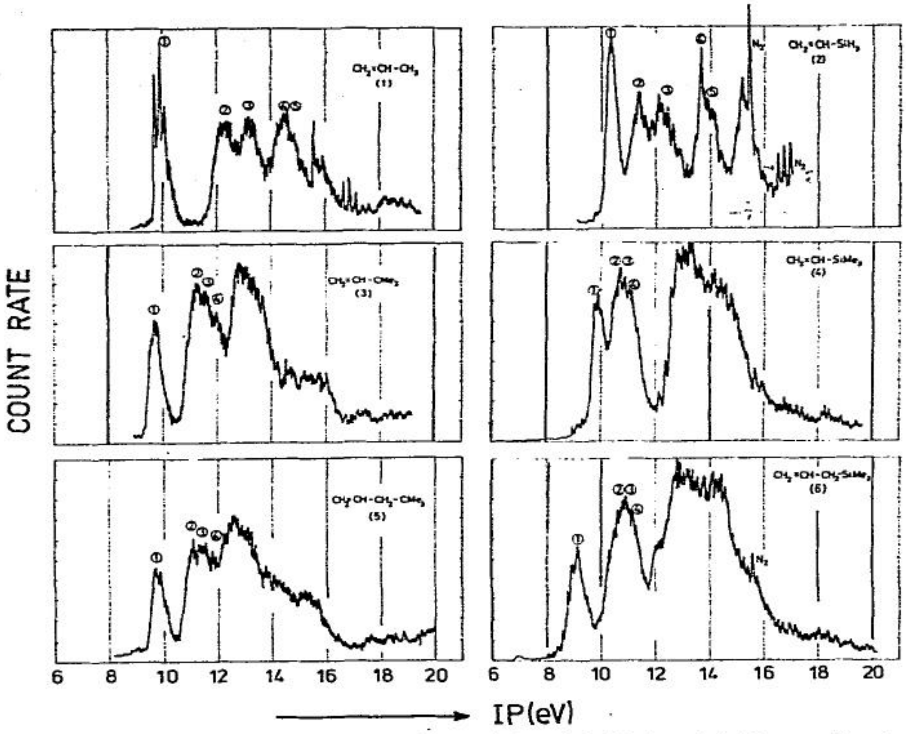

Fig. 1. Photoelectron spectra of propene (1), vinylsilane (2), 3,3-dimethyl-1-butene (3), trimethylvinylsilane (4), 4,4-dimethyl-1-pentene (5) and trimethylallylsilane (6).

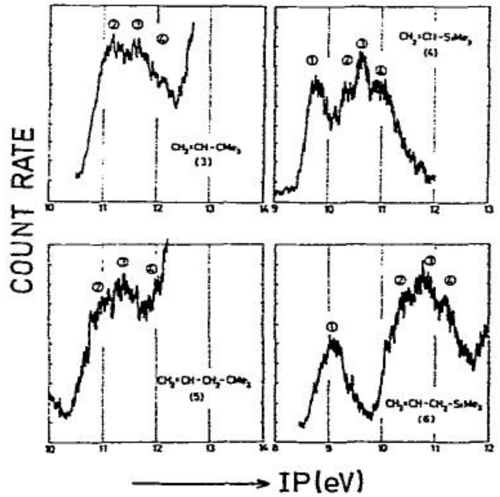

Fig. 2. Second peaks in the photoelectron spectra of 3,3-dimethyl-1-butene (3), trimethylvinylsilane (4), 4,4-dimethyl-1-pentene (5) and trimethylallylsilane (6) shown on an expanded scale.

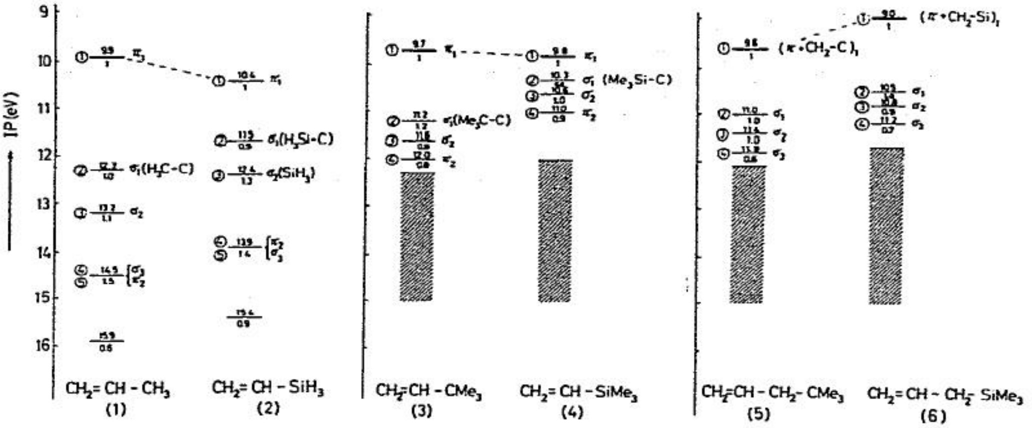

Fig. 3. Observed vertical ionization potentials (numbers printed above the levels [eV]), relative intensities (numbers below the levels) and assignment of the first four peaks (bands 1 to 5 in the photoelectron spectra of propene (1), vinylsilane (2) and the first two peaks (bands 1 to 4) in the spectra of 3,3-dimethyl-1-butene (3), trimethylvinylsilane (4), 4,4-dimethyl-1-pentene (5) and trimethylallylsilane (6).

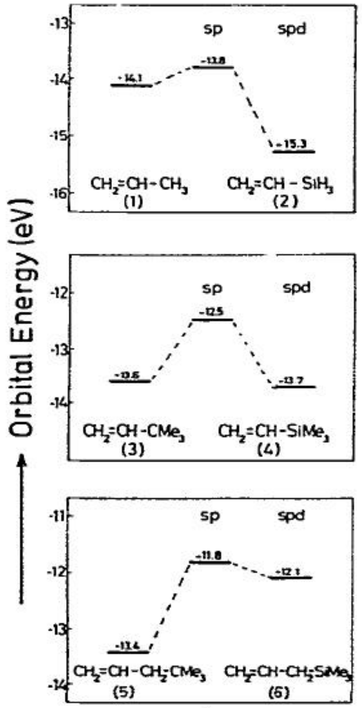

Fig. 4. Orbital energies of the π_1 HOMO of propene (1), vinylsilane (2), 3,3-dimethyl-1-butene (3), trimethylvinylsilane (4), 4,4-dimethyl-1-pentene (5) and trimethylallylsilane (6). In the case of the silicon compounds the calculations were performed on an *sp* and an *spd* basis.

CH_3 group) is followed by a $\sigma(\sigma_1)$-MO mainly localized in the C–CH_3 bond. Then after two further $\sigma(\sigma_2$ and $\sigma_3)$-MO's comes the second $\pi(\pi_2)$-MO (no node between the ethylene π-MO and the CH_3 substituent). The intensity pattern (Fig. 3) indicates that the fourth peak of (I) can be assigned to two MO's: σ_3 and π_2. Peak 1 shows vibrational structure with a spacing of 1450 cm^{-1} (C=C stretch in the molecule: 1647 cm^{-1}). The increase in the HOMO (π_1) energy in propene as compared to that in ethylene is due to C–H bond/π ethylene MO hyperconjugation.

Replacement of the methyl by the tert-butyl substituent on ethylene [*i.e.* going from compound (I) to (III)] causes quite dramatic changes in the MO energies, as the photoelectron spectra indicate (Fig. 1). Accompanying this displacement we can expect a small increase in the π-HOMO(π_1) energy, and a much more pronounced increase in the σ-MO and second π-MO(π_2) energies. The small increase of π_1 is due to C–C bond/π ethylene MO hyperconjugation in compound (III) instead of C–H bond hyperconjugation in (I) (the higher energy of the C–C bond MO leads to better energy matching with the ethylene π-MO). The pronounced energy increase of the σ-MO's (1.0–1.5 eV) in (III) is due to the higher energies which electrons in the CMe_3 group possess as compared to the CH_3 group. The bonding π-MO (π_2, no node between the ethylene π-MO and the CMe_3 substituent) is mainly localized in the CMe_3 substituent and consequently its energy must also be raised. MINDO/1 and CNDO/2 calculations yield the same order of highest occupied MO's: π_1, σ_1, σ_2, π_2. The intensity ratio of the first to the second peak (1/2.8) (Fig. 3) and the shape of the second peak, shown in Fig. 2 on a more expanded scale, indicate that this peak should be assigned to three MO's: σ_1, σ_2 and π_2. Here again, σ_1 is mainly localized in the C–CMe_3 bond (coupling σ-MO).

The substitution of CMe_3 by CH_2CMe_3 [*i.e.* going from compound (III) to (V)] leads to an interesting result. The spectra (Fig. 1 and Fig. 2) and the *IP*'s (Fig. 3) show that the MO energies of the highest occupied MO's in both compounds are very similar. Both MINDO/1 and CNDO/2 calculations indicate that this close similarity can only be reproduced for compound (V) in a conformation having the CH_2–CMe_3 bond perpendicular to the CH_2=CH molecular plane. This conformation is the most favourable for CH_2–CMe_3 σ bond/π ethylene interaction (hyperconjugation), and the HOMO is mainly an antibonding combination of both σ- and π-MO's (σ–π conjugation).

We turn now to the corresponding silicon compounds (II), (IV), and (VI) The photoelectron spectrum and the electronic structure of trimethylallylsilane (VI) has been previously[3] discussed. We note, however, that the shape and the intensity of the second peak in the spectrum suggest that this peak (bands 2, 3, and 4) should now be attributed to three MO's.

The spectrum of vinylsilane (II) consists of five peaks. Peak 1 is quite narrow with no resolved vibrational fine structure. The broader peaks 2 and 3 exhibit vibrational structure. Peak 2 show a progression with a spacing of 645 cm^{-1}. This progression is interpreted as excitation of the Si–C stretch. The corresponding vibrational frequency observed in the molecular ground state is 714 cm^{-1} [4]. Peak 3 possesses a 2036 cm^{-1} vibration, which is attributed to the Si–H stretch. In the molecular ground state this vibration is excited at 2150–2160 cm^{-1} [4]. The observed relative intensities indicate, for the first three bands at least, that each band corresponds to ionization of just one MO. These results suggest that bands 2 and 3 should be assigned to MO's mainly localized in the Si–C and Si–H bonds, respectively. The observed energy difference between the corresponding ionization potentials is 0.9 eV, in reasonable agreement with the value of 0.7 eV calculated from bond energy data[5]. The *IP* of the Si–H MO in (II) is the same as that in SiH_4 (12.4 eV)[6]. However the Si–C MO in (II) is stabilized by 1.0 eV as compared to the same MO in $Si(CH_3)_4$[7]. On the arguments above, there is no doubt about the assignment of bands 2 and 3. Therefore peak 1 must be associated with the highest occupied π-MO (one node between the ethylene π-MO and the SiH_3 group). The intensity of the fourth peak (bands 4 and 5) in (II), and the comparison with the corresponding peak in (I), suggest that this band can be attributed to ionization of two MO's: σ_3 and π_2 (no node between the ethylene π-MO and the SiH_3 substituent). CNDO/2 calculations performed on (II) both in *sp*- and *spd* basis indicate that the highest occupied MO's possess symmetry and bonding properties as expected with one exception. The Si–C MO and the π_1 MO come out in the reverse order.

Finally we consider the spectrum of trimethylvinylsilane (IV). From calculations, both π- and σ-MO's would be expected to increase in energy by nearly the same amount in going from (II) to (IV). The observed band shifts agree well with this prediction. Here again the peak shape, the measured relative intensity, and the theoretical calculations indicate that the second peak (bands 2, 3, and 4) must be attributed to ionization of three MO's, namely σ_1 (C–$SiMe_3$ coupling MO), σ_2 and π_2 (no node between the ethylene π-MO and the $SiMe_3$ substituent).

We discuss next the relationship between the MO energies in the silicon and carbon compounds. As is seen from Fig. 3 there is a close correspondence between the MO energies in the two types of molecule. In all the molecules the HOMO is the π_1-MO*. In the SiH_3 substituted ethylene [compound (II)] the π_1 energy is lower than that in the CH_3 substituted compound (I). In the ethylenes with $SiMe_3$ and CMe_3 substituents [compounds (III) and (IV)], the π_1 energies are practically the same, whereas in the corresponding ethylenes (V) and (VI) with CH_2SiMe_3 and CH_2-CMe_3 substituents the silicon compound has appreciably higher π_1 energy. These differences can be qualitatively and quantitatively understood. In all three cases because of hyperconjugation (σ–π conjugation)** the π_1 MO in the silicon compounds should exhibit considerably higher energy than the same π_1-MO in the carbon compounds. If the silicon atom is placed in α to the ethylene π-MO [as in compounds (II) and (IV)], then the d_πAO on silicon directed along the Si–C bond can bridge the π node in this bond and thus stabilize the π_1-MO. Because of this p_π–d_π conjugation, the energy of the HOMO in (II) and (IV) is considerably lowered. The two effects nearly compensate one another in (IV), whereas in (II), because of smaller hyperconjugative interaction, the p_π–d_π interaction predominates.

We previously[3] confirmed that the unusual properties of trimethylallylsilane [Compound (VI)] are clearly due to CH_2–$SiMe_3$ hyperconjugation. This σ–π con-

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* The π_1 energies of compounds (I) 9.8, (III) 9.6, (IV) 9.8 and (VI) 8.9 eV have been previously measured by mass spectrometry[8]. These values agree well with our values obtained by photoelectron spectroscopy.

** Hyperconjugation as a significant interaction mechanism between an Si–C bond and a π-system was first[9a] suggested as early as 1954. For review articles including discussions of σ–π conjugation of Si–C bonds, see ref. 9b.

jugation is much more effective than in the case of the corresponding carbon compound [compound (V)] because of the higher Si–C bond energy. Since in this case (the Si–C bond has the same direction as the p_π AO's on the ethylene carbon atoms) the position of the silicon atom is unsuited for any effective d_π bridging of the π node in π_1. Thus in compound (VI) we mainly measure by observing the change in energy of π_1 relative to (V), the corresponding change in the hyperconjugative effect.

The qualitative description of π_1 energies given above in terms of σ–π (hyperconjugation) and p_π–d_π conjugation is fully confirmed by the CNDO/2 results shown in Fig. 4. It is only by the inclusion of *d* AO's on silicon (*spd* basis) that correct π_1-MO energies for the silicon compounds (II) and (IV) relative to the analogous carbon compounds are obtained. The calculations performed on an *sp* basis (no inclusion of *d* AO's on the silicon atom) predict higher π_1-MO energies for silicon than for carbon compounds, in agreement with the σ–π conjugation model. In compound (VI), the effects of *d* AO inclusion are too small to outweigh the π_1 energy increase found on the *sp* basis. These results for the π_1 HOMO energy clearly demonstrate the importance of p_π–d_π bonding[10] in the vinylsilanes.

Fig. 3 shows that the σ-MO's and the second π (π_2)-MO in the silicon compounds are in all cases higher in energy than those in the corresponding carbon compounds [0.8–1.0 eV in compounds (II) and (IV) and about 0.6 eV in (VI)]. This difference is directly attributable to the higher Si–H and Si–C bond energies. Any mixing of the corresponding localized bond MO's into the rest of the σ bonds raises the corresponding σ-MO energies. As a further consequence, these σ-MO's are more localized in the Si–H and Si–C bonds than are the corresponding σ-MO's in the corresponding C–H and C–C bonds.

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