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A THEORETICAL STUDY OF THE EFFECT OF SILYL SUBSTITUENTS ON THE IONIZATION POTENTIALS AND ELECTRON DISTRIBUTION OF ETHYLENE

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Summary

Ab-initio SCFMO calculations have been made on ethylene, vinylsilane and allylsilane to compare the effect of silyl groups α and β to a π system. Calculations have been with a minimal basis of atomic orbitals with or without the addition of *d* orbitals of silicon. The inclusion of *d* orbitals in the basis gives a better interpretation of the photoelectron spectra than their exclusion, particularly for the α-silyl group. The *d* orbitals also make a significant contribution to the difference in energy between the configurations of allylsilane. The net atomic group charges have been calculated for the neutral molecules and their positive ions and the net loss of π electrons from the SiH_3 group on ionization is similar in vinyl and allylsilane. Vinylsilane shows a greater redistribution of σ electrons on ionization.

The substantial influence of β-(metallomethyl) substituents on the properties of unsaturated hydrocarbons has been a subject of considerable interest in view of the fact that the changes in reactivity and spectroscopic properties are in general larger for β- than for α-metallo substituents. In other words, the expected buffering effect of the CH_2 group does not occur.

The β-silyl group was first postulated to be a π-electron releasing [hyperconjugative] group by Eaborn and Parker [1] from their studies of the UV spectra of trimethylsilyl-substituted benzoic acids, and later [2], on the rate of acid cleavage of aryl—Si bonds. Traylor [3] supported this idea, after a study of the stabilization of carbonium ions, for which these substituents seem to show their largest effect.

Bock and Alt [4], in a study of the charge-transfer spectra of β-silyl substituted benzenes with TCNE complexes, deduced that the β-silyl group lowered the π-ionization potential through a substantial +*I* (inductive) effect. However, from later work on the photo-electron (PE) spectra of substituted ethylenes, Mollere et al. [5] concluded that inductive effects and hyperconjugation, involving both σ(C—Si)—p_π and d(Si)—p_π mixing, were necessary for a proper understanding of the experimental data. What is not in doubt, from studies of the charge transfer bands with TCNE (and by inference the ionization potentials) of sterically rigid molecules [6, 7], is that the substituent effect is sensitive to the relative orientation of the C—Si bond and the plane of the π-electron system. From this one would normally infer that hyperconjugative effects played an important role in determining the electronic energies.

A substantial hyperconjugative effect is also suggested by the observation that the ESR spectra of carbon π-radicals with β-(metallomethyl) substituents show large hyperfine coupling to the β atoms [8]. It has been deduced that the radicals all have a conformation in which the metal is constrained above the π-electron plane so that overlap of the C—Si σ orbital and the π orbitals of the ring is maximized.

Weidner and Schweig in their analysis of the PE spectrum of allyltrimethylsilane [9], deduced that the substituent adopted a conformation that maximized hyperconjugation, and they later used this procedure to deduce the conformations of Ge and Sn β substituents [10]. Mollere et al. [5], on the other hand, concluded that for the allylsilanes there was free rotation about the C—Si bond.

Theoretical studies on the β-silyl effect have been confined to qualitative molecular orbital arguments and semi-empirical studies of the CNDO type. However, the lack of satisfactory parametrization for second-row elements in these models make deductions from such calculations of doubtful reliability. We shall show in this paper that some of the conclusions drawn from the semi-empirical calculations are not substantiated by ab-initio calculations.

Method of calculation

Calculations were based on the SCFMO method using the ATMOL system of programs of the ATLAS computer laboratory. A minimal basis of Slater atomic orbitals was chosen with the inclusion of silicon 3d orbitals. The following orbital exponents were used:

> For carbon 5.70 (1s), 1.625 (2s, 2p) and for the attached hydrogens 1.20 (1s).
> For silicon and its attached hydrogens we adopted the optimized silane exponents of Boer and Lipscomb [11] * 13.57 (1s), 4.5 (2s), 4.97 (2p), 1.6 (3s), 1.43 (3p), 1.30 (3d), and for the hydrogens 1.26 (1s).

Each Slater orbital was expanded with three gaussian lobe functions according to the criterion of Stewart [12]. With such a small gaussian expansion the total energy will be relatively poor because of an inaccurate representation of the inner shells, but the relative energies should be accurate.

The addition of d orbitals to a minimal valence basis has the dual role of giving added flexibility in the radial and angular parts of the wave function. It

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* The exponents quoted by Boer and Lipscomb [11] had five significant figures and these were used in the calculation. We do not, however, wish to impute any significance to the last two figures.

is well known that *d* orbitals appear more important in such a calculation than when they are added to an extended basis of valence orbitals.

Calculations have been performed on allylsilane which is the simplest example of a silyl substituent β to a planar π-system. For comparison with the equivalent hydrocarbons and with the α substituents we have also made calculations on 1-butene, vinylsilane, propene and ethylene. For the β groups two configurations have been considered. In one, the β-atom (Si or C) was in the plane of the ethylene nuclei with the C—Si (or C—C) bond *trans* to the double bond. In the other the β group was rotated to its maximum displacement from this plane. We will refer to these as the parallel and the perpendicular configurations respectively.

Experimental geometries were used for the calculations on ethylene and propene [13]. For the other molecules which lack an experimental geometry we adopted the following parameters:

r(C—H) = 1.07 Å, r(C=C) = 1.337 Å (as in ethylene)
r(C—Si) = 1.865 Å (as in CH_3—SiH_3)
r(C—C) = 1.488 Å (α to the double bond, as in propene)
r(C—C) = 1.541 Å (β to the double bond)
r(Si—H) = 1.480 Å (as in silane)

The angles were taken as 120° at the double bond and tetrahedral elsewhere.

A parameter that we suspected to be important in the calculation was the length of the α C—C bond, which in propene is appreciably shorter than the bond between sp^3 carbon atoms. It would be a reasonable assumption to suppose that the α bond is also short in 1-butene and allylsilane. To confirm this we calculated the energies of propene and butene for five values of the α C—C bond length and found in both cases the same equilibrium bond length, namely 1.56 Å. Our calculation therefore does not reproduce the short α bond (which is probably because our gaussian expansion is relatively poor) but does suggest that the same bond length should be used for both molecules. Moreover, the molecular orbital energies were not sensitive to the length of the α C—C bond so we made no attempt to optimise this bond length for the β-silyl compounds, but used the same short value 1.488 Å as in propene.

Tables 1 and 2 show the total energies and occupied orbital energies above —21 eV for all compounds and configurations considered. We also include the energy of the lowest vacant (virtual) orbital. The orbitals whose energies are below —21 eV are predominantly composed of carbon 2*s*, silicon 3*s* and the inner orbitals, and will not be observed in a HeI photoelectron spectrum.

From the data of Tables 1 and 2 and other aspects of the calculations we have selected the following points as being most worthy of note.

1. The effect of including *d* orbitals in the basis

The inclusion of *d* orbitals in the basis lowers the total energy of the silicon compounds substantially and lowers the orbital energies by amounts significant in comparison with the shifts relative to ethylene. For the β substituents the inclusion of *d* orbitals increases the difference in the energy between the parallel and perpendicular configurations.

TABLE 1

ORBITAL ENERGIES (eV) AND TOTAL ENERGIES (a.u.) FOR ETHYLENE, PROPYLENE AND VINYLSILANE

π symmetry orbitals have been identified to assist in the correlation of orbitals of different molecules.

Ethylene	Propylene	Vinylsilane (without *d*)	Vinylsilane (with *d*)
7.03 (π^*)	7.05 (π^*)	6.63 (π^*)	5.28 (π^*)
−9.98 (π)	−9.32 (π)	−9.52 (π)	−9.90 (π)
−13.31	−12.95	−11.37	−11.68
−15.24	−13.79	−12.62	−12.89
−17.12	−15.55	−13.09 (π)	−13.24 (π)
−21.15	−15.62 (π)	−14.68	−14.96
	−17.13	−16.46	−16.74
	−20.23	−18.95	−18.79
Total energies			
−77.7641	−115.6049	−363.8363	−363.9314

The fact that the *d* orbitals lower the total energy of the β compounds to a large extent but have only a small effect on the ionization potential or the parallel-perpendicular energy difference shows that they modify substantially the wave functions locally around the silicon atom but that there is rather little *d* orbital mixing with the ethylene π orbitals. The *d* orbitals lower the π orbitals of vinylsilane significantly more than those of allylsilane showing that the d—π mixing is greater for α than for β silyl groups as expected.

The *d* orbitals make their largest contributions to the virtual $\pi^\star$ orbitals which are not relevant to the photoelectron spectra but would be involved in the interpretation of UV spectra. We have included only the energy of the first virtual orbital in Tables 1 and 2, because of the expected strong contribution of the first excited configuration to the wave function of the first π—$\pi^\star$ excited state.

The reduction of 1.343 eV in the energy of the $\pi^\star$ orbital of vinylsilane by inclusion of *d* orbitals in the basis far exceeds the reduction of 0.385 eV in the π orbital and we would conclude that the observed lowering of the π—$\pi^\star$ transition of ethylene by an α silyl group, which is approximately 0.8 eV, is substantially associated with the delocalization of the $\pi^\star$ orbital into the *d* orbitals of the silicon atom.

The PE spectrum of vinylsilane shows that an α silyl substituent produces almost no shift in the first PE band of ethylene and this is in accord with our calculations only if *d* orbitals are included in the basis. It appears therefore that *d* orbitals have an important bearing on the interpretation of the electronic spectroscopy of silyl substituents, at least when a minimal basis of valence orbitals is used, and we will confine further comments to those calculations which include *d* orbitals in the basis.

2. The difference between the parallel and perpendicular configurations of the β substituents

The results of Table 2 show clearly that there is a larger difference between the energy of the two configurations for allylsilane than for 1-butene.

TABLE 2

ORBITAL ENERGIES (eV) AND TOTAL ENERGIES (a.u.) FOR ALLYLSILANE AND 1-BUTENE

The designation π is not strictly valid for the perpendicular configurations but it has been used to identify orbitals with a large contribution of $2p_z$ atomic orbitals of the three carbon atoms.

Allylsilane				1-Butene	
Parallel configuration		Perpendicular configuration		Parallel configuration	Perpendicular configuration
Without *d*	With *d*	Without *d*	With *d*		
7.06 (π^*)	6.70 (π^*)	7.04 (π^*)	6.33 (π^*)	7.06 (π^*)	7.07 (π^*)
− 9.44 (π)	− 9.62 (π)	− 8.99 (π)	− 9.22 (π)	− 9.34 (π)	− 9.34 (π)
−11.29	−11.61	−12.09	−12.38	−12.52	−12.53
−12.22	−12.55	−12.23	−12.59	−12.98	−12.81
−12.34 (π)	−12.70	−12.41 (π)	−12.72 (π)	−13.44 (π)	−13.78 (π)
−13.15	−13.32	−13.64	−13.80	−14.12	−14.49
−15.33	−15.47	−14.05	−14.18	−16.06	−15.17
−15.56 (π)	−15.68 (π)	−15.47	−15.62	−16.58 (π)	−16.22
−16.45	−16.59	−17.06	−17.23	−16.68	−17.47
−19.18	−18.89	−18.99	−18.70		
−20.30	−20.45	−20.34	−20.47		
Total energies					
−402.3950	−402.4856	−402.3983	−402.4907	−154.1641	−154.1658
Total energies of positive ion					
	−402.1758		−402.1914		

The energy difference for 1-butene is calculated to be only 4 kJ/mole and so for the molecule the free-rotating model as adopted by Mollere et al. [5] for their interpretation of the PE spectrum would seem to be valid. For the β-silyl group the difference is approximately 13 kJ/mole and at room temperature this would give a Boltzmann distribution of less than 1% in the parallel configurations, confirming the deduction of Weidner and Schweig [9] from the PE spectrum that the compound adopts the perpendicular configuration. Mollere et al. [5] on the other hand assumed free rotation for both allylsilane and 1-butene in their interpretation of the PE spectra.

If one adopts the procedure of measuring the relative importance of σ—π hyperconjugation and inductive effects by the difference between the parallel and perpendicular configurations (as is done by Radom et al. [14]) then we have already noted that this difference is larger for the silyl than for the alkyl compound. However, this cannot be said to give an absolute measure of the hyperconjugative effect because of the contributions from both C—H and C—C or C—Si hyperconjugation. For 1-butene we deduce either that the inductive effect dominates the shift of approximately 0.6 eV in the first PE band of ethylene or that C—H and C—C hyperconjugation are almost equal in importance.

The calculated shift in the first PE band of ethylene arising from the β substituents is smaller for allylsilane than for 1-butene in the parallel configuration but larger for the perpendicular configuration. As the latter accords with experiment we deduce, as do Weidner and Schweig [9], that the conformation of the silyl group is important in interpreting the spectrum of allylsilane. We further conclude that the shift in the PE band is dominated by the hyperconjugation of the C—Si bond orbital and the earlier supposition that the inductive effect of the β-silyl group played a dominant role is definitely wrong.

3. The PE spectra of the α compounds

Figure 1 shows the PE spectra of all compounds calculated in this study [5]. The predicted energies are based on Koopmans' theorem that the ionization potential is the negative of the SCF orbital energy. Of the predicted four bands of ethylene absolute agreement between calculated and observed energies is poorest for the highest energy band, which is in error by approximately 1.0 eV.

The predicted change in the PE spectra on introducing the methyl or silyl group is reproduced more accurately by our calculations than the absolute positions of the bands. The first (π) band is predicted to be lowered in energy by 0.65 eV by the methyl substituent and the observed shift is approximately 0.6 eV. For the silyl compound both prediction and experiment show almost no shift in the π band.

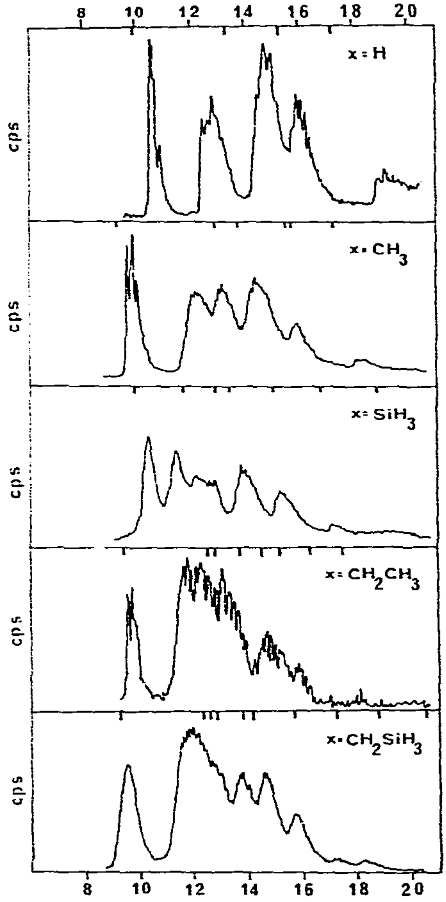

Fig. 1. The photoelectron spectra of ethylene, propene, vinylsilane, 1-butene and allylsilane. The molecular orbital energies given in Tables 1 and 2 are indicated by the vertical lines above each figure.

The lower energy orbitals for vinylsilane are all above the corresponding orbital of propylene. This situation is found generally when one compares silanes and alkanes (SiH_4 and CH_4 for example) and is due to the fact that the ionization potentials of the silicon valence orbitals are less than those of the corresponding carbon valence orbitals. To assign the bands in the PE spectra of both propene and vinylsilane we have assumed that, as for ethylene, the calculated ionization potentials will be greater than the observed, with the difference increasing as the orbital energies decrease. Our assignment for propene is identical with that of Weidner and Schweig [9] which was based on MINDO/1 and CNDO/2 calculations but differs from their interpretation of vinylsilane in that we associate the second ionization potential with the band at approximately 13 eV rather than that at 14 eV.

4. The PE spectra of the β compounds

The position of the first PE band of the β compounds relative to ethylene is well represented by our calculations, providing that we adopt the perpendicular configuration for the silyl compound. From the parallel configuration we would predict that the silyl compound had a higher energy PE band than 1-butene. The separation between the first and second PE bands is also well represented by the calculations, being, in contrast to the α silyl compound, similar to that in ethylene.

Our calculations suggest, as the spectra indicate, that the second region of the PE spectra of the β compounds is complex and due to an overlap of three or four bands. In making an assignment it is appropriate to assume that, as for ethylene, our calculations overestimate the energies of the higher energy PE bands.

5. Calculations on the positive ions

Our interpretation of the PE spectra has so far been based upon the use of Koopmans' theorem. This will be in error in two respects. Firstly there will be some reorganisation of the electrons in the positive ion after ionization and secondly the correlation energy between electrons in the same molecular orbital (which is not represented by MO theory) is less in the positive ion than in the neutral molecule. The first effect will lead to an overestimation and the second to an underestimation of the ionization potential by the use of Koopmans' theorem. It is probably the balance of these two errors that makes Koopmans' theorem a generally satisfactory basis for the calculation of ionization potentials.

It has been stated by Traylor et al. [3] and by others that the hyperconjugative effect is only developed to an appreciable extent in the positive ion, and this would imply that the transfer of electrons from the β-silyl group to the double bond was much greater for the positive ion than for the neutral molecule. To test this hypothesis we have made unrestricted SCFMO calculations on the ground state of the positive ions of ethylene, vinyl and allylsilane (perpendicular configuration) and compared the electron distribution and ionization potentials obtained in this way with those based upon Koopmans' theorem. The electron densities are defined by the Mulliken population numbers which

TABLE 3

NET ATOMIC GROUP CHARGES (q) OF VINYL AND ALLYLSILANE AND THEIR POSITIVE IONS AND A COMPARISON OF THE ELECTRON DENSITY CHANGE ON IONIZATION WITH THE POPULATION (p) OF THE HIGHEST OCCUPIED MOLECULAR ORBITAL OF THE NEUTRAL MOLECULES

The olefine carbon atoms are listed first.

	q	q^+	Δq	Δq_σ	Δq_π	p
Vinylsilane						
CH_2	0.028	0.434	0.406	−0.001	0.407	0.460
CH	−0.112	0.174	0.286	−0.213	0.499	0.438
SiH_3	0.084	0.392	0.308	0.214	0.094	0.102
Allylsilane						
CH_2	−0.024	0.371	0.395			0.454
CH	0.012	0.307	0.295			0.334
CH_2	−0.089	0.036	0.125			0.116
SiH_3	0.101	0.287	0.186			0.096

allow for the distribution of orbital-overlap densities to the two atoms making up the bond.

A direct comparison of the individual atom population densities of molecule and positive ion is confused by the substantial relaxation of charge that occurs in the C—H and Si—H bonds on ionization. Our calculations on the positive ions show that on ionization approximately 0.1 units of electron density is removed from the hydrogen attached to the olefine carbon atoms. To have densities that compare more directly quantities of chemical interest we have therefore shown in Table 3 the net charges of the carbon and silicon atoms and their attached hydrogens. A further advantage of this procedure is that it is more likely to give charges which are independent of the detailed ionic character of the C—H and Si—H bonds. With our basis we find, like Boer and Lipscomb [11], that Si—H bonds are polarized with the hydrogen having a positive charge of about 0.11 units. However, Liskow and Schaefer [15], using a more extensive basis, obtained a negative charge of 0.20 on the hydrogens. For both bases however the SiH_3 group is positive with respect to CH_3 in methylsilane.

The calculations show that on ionization of vinylsilane there is a considerable migration of electrons from the SiH_3 to the neighbouring CH but this is mainly through the σ system. A comparison of p (which measures the loss of electrons from the π system with all other electrons frozen) and Δq (which allows for relaxation of the other electrons) shows that there is some relaxation of π electrons in the C=C bond but no enchanged π migration from the SiH_3; a small reverse trend is in fact observed.

For allylsilane there is no exact symmetry separation into π and σ so that only the total q is rigorously defined. However, if we take the quantity p as being a rough measure of the electron loss from near —π symmetry orbitals then the difference between this and Δq shows that there is again some shift in the σ system on ionization but the total transfer from the substituent group to the olefine is only of the order of 0.1 units, considerably less than for vinylsilane.

Our calculations therefore suggest that the total π electrons of the β silyl group are more effectively delocalized to the olefine systems than for the α silyl although those of the silicon are approximately the same in both cases. The σ electrons of the α-silyl group are, however, much more influenced by changes in the π electron density of the olefine than are the σ electrons of the β group. Calculations on these systems without *d* orbitals show smaller electron densities on the SiH_3 for both neutral molecule and ion but the differences Δq are very little changed.

We have seen from Koopmans' theorem that the calculated shift in the first ionization potential of ethylene is —0.08 eV for the α and —0.76 eV for the β substituent. By taking the ionization potential as the difference in the ground state energies of the molecule and positive ion, we find these shifts to be —0.33 eV and —0.63 eV for the α and β substituents respectively.

The ionization potential of ethylene itself was found to be 9.05 eV when calculated from the difference in ground state energies which is 0.93 eV less than is given by Koopmans' theorem and definitely poorer when compared with the experimental value 10.5 eV. In other words the ionization potentials both absolutely and in their differences are reproduced better by the use of Koopmans' theorem than by the difference of total molecular energies.

6. Conclusions

The ab-initio calculations with a minimal basis of valence orbitals supplemented by *d* orbitals of the silicon give a satisfactory interpretation of the PE spectra of the substituted ethylenes. The *d* orbitals modify the orbital energies by amounts significant when compared with measured substituent shifts in ionization potentials and they modify the parallel-perpendicular energy difference for allylsilane by an amount significant for the calculation of the equilibrium population of the two structures. One might therefore be tempted to deduce that *d* orbitals are important for an understanding of the spectroscopic and ground state properties of silyl-substituted ethylenes. This deduction must however be qualified by the statement made earlier that *d* orbitals, when added to a minimal basis, produce a greater effect than when added to an extended valence basis. Nevertheless, the provision of some functions in the basis of the silicon atom which interact strongly with the virtual $\pi^\star$ orbitals of ethylene do appear to be important for a satisfactory interpretation of the spectroscopic data.

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