Photoelectron Spectra and Molecular Properties. XXX.[1]
π Interactions in H_3Si- and H_3C-Substituted Acetylenes

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Abstract: The photoelectron (pe) spectra of mono- and disubstituted silyl- and methylacetylenes are assigned by comparison with the corresponding ionization potentials of acetylene, disilane, and ethane. The observed π splittings can be rationalized within a parameterized hyperconjugation model. Calculations using a modified CNDO/2 procedure with and without inclusion of 3d orbitals in the basis set demonstrate that the usual parameters tend to overemphasize $p_\pi d_\pi$ back-bonding. To rationalize available experimental data, $3d_{Si}$ orbitals need not to be considered explicitly—neither for the different dipole moments of methyl- and silylacetylenes nor for the general pe spectroscopic pattern of silicon compounds, *i.e.*, high first ionization potential, reduced spin–orbit coupling, or band broadening.

The cylindrical π system of acetylene and its perturbation by substituents have been the subject of numerous investigations. In particular, the different properties of trimethylsilyl- and *tert*-butylacetylenes[3] have been attributed to differences in inductive and conjugative effects of silyl and alkyl groups. In contrast, Pitt,[4] on the basis of CNDO/2 calculations, proposed a hyperconjugative model neglecting $p_\pi d_\pi$ back-bonding to account for silicon substituent effects. Heilbronner, *et al.*,[5] completely assigned the photoelectron spectra of trimethylsilylacetylene and its halogen derivatives and derived spectroscopically basis orbital parameters for the trimethylsilyl group. In the following we report the assignment and interpretation of the photoelectron spectra of silyl- and methylacetylenes $H_3XC{\equiv}CH$ and $H_3XC{\equiv}CXH_3$ (X = C, Si).

Pe Spectra and Hyperconjugation Model

The spectra of the four silyl- and methyl-substituted acetylenes are shown in Figure 1, and their vertical ionization potentials are compiled in Table I.

Based on Koopmans theorem[6] the pe spectrum of acetylene[7] has been interpreted in terms of the orbital sequence $(1\pi_u)^4$ $(3\sigma_g)^2$ $(2\sigma_u)^2$. The first band, corresponding to electron ejection from the doubly degenerate π_u orbital, consists of well-resolved peaks with ΔIP = 1830 cm^{-1}, the small reduction relative to the ground-state C≡C stretching frequency $\nu_{C\equiv C}$ = 1983 cm^{-1} indicating only a modest change of the triple bond lengths in the radical cation.

In the pe spectrum of methylacetylene[7] (Figure 1), the first pe band rises steeply and clearly displays the acetylene π vibrational fine structure ($\nu_{C\equiv C}$: ion, 1940 cm^{-1}; ground state, 2142 cm^{-1}). In contrast, the π band of silylacetylene (C_{3v}: 2e) is shifted to higher ionization potential and considerably broadened and its vibrational spacing ($\nu_{C\equiv C}$: ion, 1760 cm^{-1}; ground state,[8] 2192 cm^{-1}) is less pronounced. Such differences are frequently observed for alkyl–silyl exchange at π[9] or lone pair centers[10] and are attributed to increasing π-type delocalization.[6] At higher ionization potentials three pe bands are observed for methylacetylene and six for the silyl compound. Obviously, the ionization energies of silylacetylene except the first one are more or less lowered relative to those of methylacetylene (Figure 1 and Table I).

For a complete assignment we use a qualitative hyperconjugation model based on linear combinations of bond orbitals (LCBO) as specified in Figure 2. Applying second-order perturbation arguments to each set of symmetry equivalent basis orbitals yields a qualitative orbital sequence, in which one σ orbital, $4a_1$, is inserted between the π orbitals 2e and 1e, resulting from hyperconjugative mixing and characterized by a nodal plane in the threefold molecular axis. Within the LCBO MO model, the hyperconjugative interaction in methylacetylene can be parameterized identifying the energy of the basis orbital $e_{C\equiv C}(\pi)$ with the first vertical ionization potential of acetylene $IP_\pi{}^v$ = 11.40 eV and $e_{XH_3}(\pi)$ with the center of gravity of the ionization potentials of either the orbital pair e_g/e_u of H_3XXH_3 or the t_2 orbitals of XH_4. For the parameterization of the silylacetylene hyperconjugation model, we start with disilane, the pe spectrum[11] of which shows two Jahn–Teller split bands, $1e_g$ and $1e_u$, at 11.88–12.13 and 12.73–13.08 eV. From the average value $e_{SiH_3}(\pi)$ = 12.45 eV and the acetylene π ionization potential $e_{C\equiv C}(\pi)$ = 11.40 eV, we obtain as the π center of

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(1) Part XXVIII: K. Wittel and H. Bock, *Chem. Ber.*, **107**, 317 (1974).

(2) W. Ensslin, Thesis, University of Frankfurt, 1974.

(3) H. Bock and H. Seidl, *J. Chem. Soc. B*, 1158 (1968), and literature quotations given therein.

(4) C. G. Pitt, *J. Organometal. Chem.*, **61**, 49 (1973), and literature quotations given therein.

(5) G. Bieri, F. Brogli, E. Heilbronner, and E. Kloster-Jensen, *J. Electron Spectrosc. Relat. Phenomena*, **1**, 67 (1972).

(6) *Cf.* for instance C. R. Brundle and M. B. Robin in "Determination of Organic Structures," Vol. III, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971.

(7) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(8) H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer, Berlin, 1966, and literature quotations given therein.

(9) *Cf.* for instance P. Mollère, H. Bock, G. Becker, and G. Fritz, *J. Organometal. Chem.*, **46**, 89 (1972).

(10) *Cf.* for instance S. Cradock and E. A. V. Ebsworth, *Chem. Commun.*, 57 (1971); S. Cradock and R. A. Whiteford, *Trans. Faraday Soc.*, **67**, 3425 (1971); *J. Chem. Soc., Faraday Trans. 2*, **68**, 281 (1972); H. Bock, P. Mollère, G. Becker, and G. Fritz, *J. Organometal. Chem.*, **61**, 113, 127 (1973).

(11) H. Bock, W. Ensslin, F. Feher, and W. Freund, unpublished results.

Table I. Vertical Ionization Energies (eV) of Methyl- and Silylacetylenes, Acetylene, Ethylene, and Disilane

Compd	$\pi_{C\equiv C}$	1	2	3	4	5	6
$H_3CC\equiv CH$[6]	10.37		14.6	$\left(\begin{matrix}15.3\\15.5\end{matrix}\right)_{sh}$	17.4		
$H_3SiC\equiv CH$	10.73		12.53	$\left\{\begin{matrix}13.05\\13.85\end{matrix}\right\}^{a}_{J/T}$	17.4	18.9	20.4
$H_3CC\equiv CCH_3$[23]	9.61		$(14.0)_{sh}$	14.5	$(15.0)_{sh}$	$(15.8)_{sh}$	20.63
$H_3SiC\equiv CSiH_3$	10.46		$(12.4)_{sh}$	12.9	14.51	18.2	19.0
$HC\equiv CH$[7]	11.40		16.75	18.75			
H_3CCH_3[7]		12.1	$\left\{\begin{matrix}12.7\\13.25\end{matrix}\right\}^{a}_{J/T}$	$\left\{\begin{matrix}15.5\\15.7\end{matrix}\right\}^{a}_{J/T}$	20.5		
H_3SiSiH_3[2]		10.53	$\left\{\begin{matrix}11.88\\12.13\end{matrix}\right\}^{a}_{J/T}$	$\left\{\begin{matrix}12.73\\13.08\end{matrix}\right\}^{a}_{J/T}$	16.5		

[a] J/T: pe bands obviously split by the Jahn–Teller effect (see text).

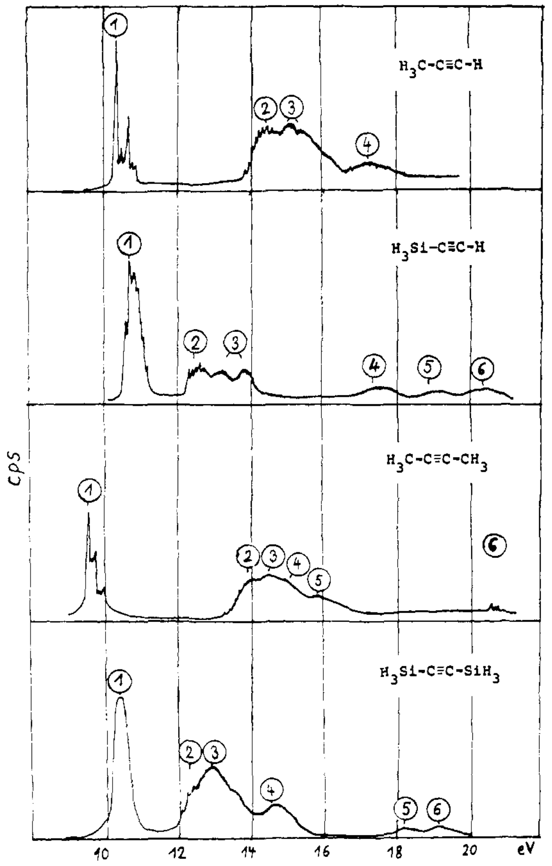

Figure 1. Pe spectra of mono- and disubstituted methyl- and silylacetylenes.

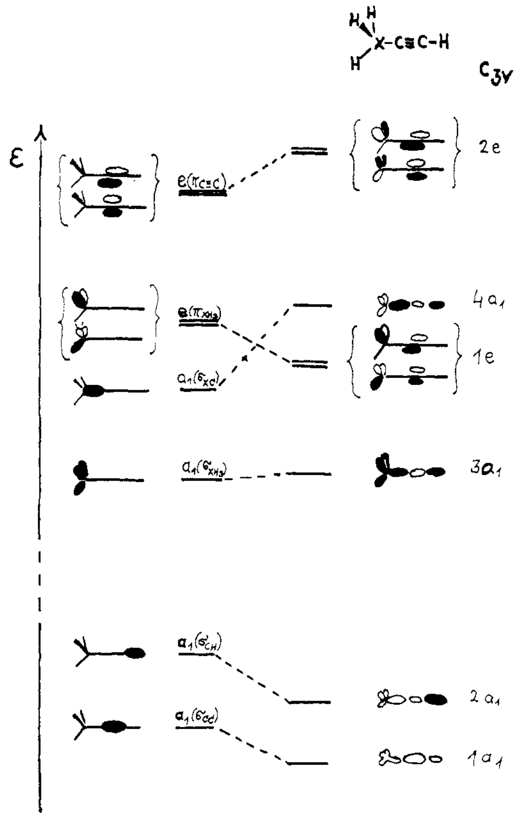

Figure 2. LCBO MO model for monosubstituted acetylenes $H_3XC\equiv CH$.

gravity $\overline{e(\pi)}$ = 11.93 eV. In the pe spectrum of silylacetylene (Figure 1) the corresponding mean, $\overline{e(\pi)}$ = $[e_{SiH_3}(\pi) + e_{C\equiv C}(\pi)]/2$ = (13.45 + 10.73)/2 = 12.09 eV, is shifted by +0.16 eV, probably because all unoccupied orbitals are neglected[12] within the LCBO MO model (see Figure 2). This value is used to correct the basis orbital energies $e_{SiH_3}(\pi)$ = 12.45 + 0.16 = 12.61 eV and $e_{C\equiv C}(\pi)$ = 11.40 + 0.16 = 11.56 eV, henceforth called coulomb parameters $\alpha_{C\equiv C}$ and α_{XH_3}. The LCBO interaction term, *i.e.*, the resonance integral $\beta_{\pi,H_3SiCCH}{}^{LCBO}$, is then calculated from the corresponding second-order determinant to be −1.25 eV. Analogously, with $e_{CH_3}(\pi)$ = 14.25 eV ($\bar{e}$ (ethane) = 14.3 eV and $\bar{t}_2$ (methane) = 14.2 eV[13]) one obtains for methylacetylene a hyperconjugation parameter $\beta_{\pi,H_3CCCH}{}^{LCBO}$ = −2.07 eV. As shown subsequently, these $\beta_\pi{}^{LCBO}$ values allow calculation of the π ionization potentials of dimethyl- and disilylacetylenes as well.[14] Therefore, the pe spectra of the monosubstituted acetylenes are tentatively assigned following the proposal in Figure 2. The second pe band corresponds to an ionization from the σ orbital 4a₁ mainly representing the X-C bond, which is supported by the 2 eV reduction on methyl–silyl exchange or by the vibrational fine structures (*e.g.*, silyl deformation:[8] ground state, 936 cm^{-1}; ion, 890 cm^{-1}). The third band is due to electron ejection from the degenerate H_3X orbital 1e in accordance with the observed Jahn–Teller split and with the lack of vibrational fine structure. It is

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(12) *Cf.*, *e.g.*, M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973); H. Bock, J. Sauer, D. Seebach, G. Wagner, and K. Wittel, *Chem. Ber.*, in press.

(13) A. W. Potts and W. C. Price, *Proc. Roy. Soc., Ser. A*, **326**, 165 (1972).

(14) For restrictions, see F. Brogli, E. Heilbronner, V. Hornung, and E. Kloster-Jensen, *Helv. Chim. Acta*, in press.

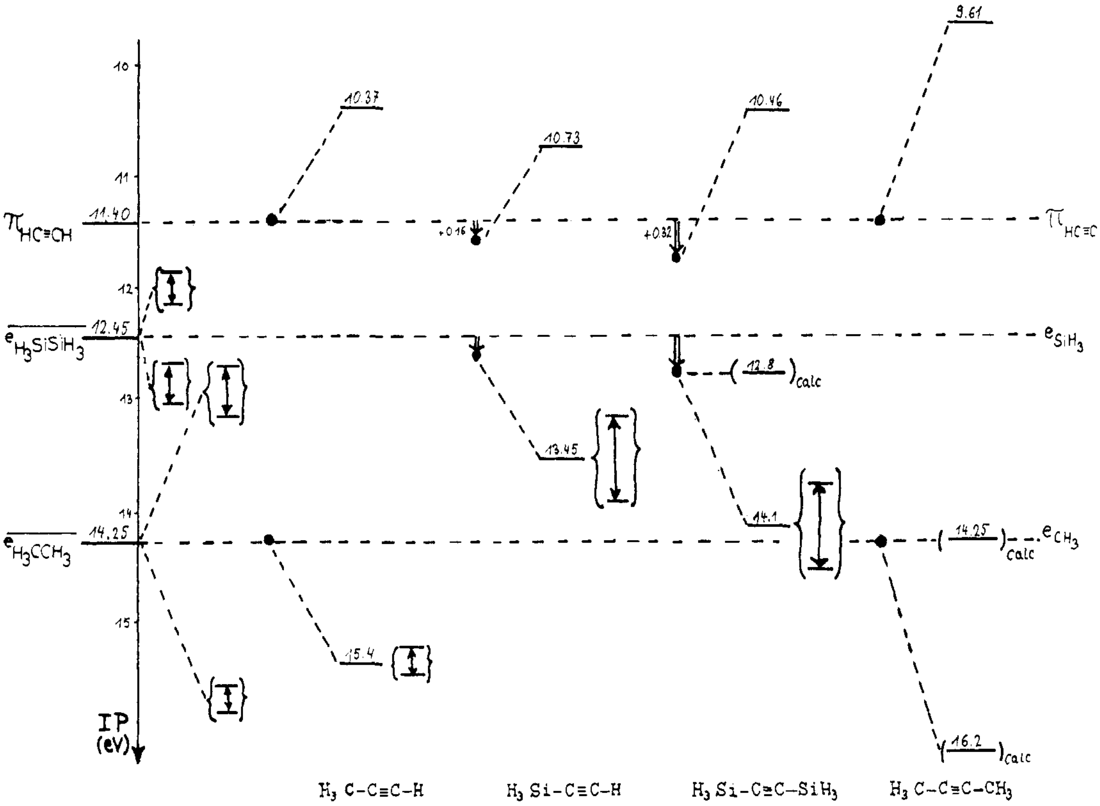

Figure 3. Hyperconjugation model for methyl- and silylacetylenes, including center of gravity corrections (↓) as well as pe ionization potentials of the e(π) assigned bands. Observed Jahn–Teller splits are indicated by { } and assignments of overlapping bands according to parameterization by $(\ )_{\text{calc}}$.

lowered in the silyl derivative by 2 eV. In contrast the fourth band stays almost constant representing more or less the acetylene C–H bond $3a_1$.

The parameter β_π^{LCBO}, calculated from $H_3XC{\equiv}CH$ ionization potentials, will now be utilized to assign the $H_3XC{\equiv}CXH_3$ pe spectra. To do so, our model has to be expanded for two e_{XH_3} basis orbitals, assuming free rotation in the $H_3XC{\equiv}CXH_3$ molecules and therefore the D_3 conformation being the most frequent one. From the linear combinations of the two e_{XH_3} group orbitals

$$\phi_{XH_3}{}^{\pm} = \frac{1}{\sqrt{2}}(\phi_1(e_{XH_3}) \pm \phi_2(e_{XH_3})) \qquad (1)$$

only $\phi_{XH_3}{}^{+}$ will interact with the acetylene π orbital $\phi_{C\equiv C}$. Therefore only a split $\phi_{XH_3}{}^{+}/\phi_{C\equiv C}$ is to be expected, whereas $\phi_{XH_3}{}^{-}$ should remain unaffected. Starting with the coulomb parameters $\alpha_{C\equiv C} = -11.72$ eV (again corrected by +0.16 eV) and $\alpha_{SiH_3} = -12.77$ eV and with the interaction term $\beta_{\pi,H_3SiCCSiH_3}{}^{LCBO} = \sqrt{2}\beta_{\pi,H_3SiCCH}{}^{LCBO} = \sqrt{2}(-1.25) = -1.77$ eV, one calculates for disilylacetylene the π-orbital energies $\epsilon_{1,2} = -12.24 \pm 1.84$ eV. Of the resulting two eigenvalues, $\epsilon_1 = 10.4$ eV matches perfectly with the observed π ionization potential $IP_\pi{}^{v} = 10.46$ eV (Table I). For dimethylacetylene one also finds a near perfect matching of the experimental $IP_\pi{}^{v} = 9.61$ eV with the value 9.62 eV, calculated analogously by inserting the monomethylacetylene parameters $e_{C\equiv C}(\pi) = 11.40$ eV and $e_{CH_3}(\pi) = 14.25$ eV. The second and third π-orbitals are then expected at about 14.25 eV (nonbonding) and at about 16.18 eV (bonding), the other value obtained from the above calculation.

The results of the parameterized hyperconjugation model are displayed in Figure 3, together with the vertical ionization energies of those pe bands, which will be assigned to the e(π) orbitals.

The assignment of the less well-resolved part of the disilyl- and dimethylacetylene pe spectra starts advantageously from the three e(π) orbitals (Figure 3). As the lowest π ionization potential is well reproduced by the parameterization, the two higher ones are also considered trustworthy. Modified CNDO/2 calculations yield the orbital sequence $3e < 3a_1 < 2e < 1e < 2a_2 < 2a_1 < 1a_2 < 1a_1$ (*cf.* Figure 4).

Although intensity ratios are generally[6] considered a rather poor guideline in assigning pe spectra, the linearly corrected values for the first three bands of disilylacetylene approaching 2:5:2 would fit to the CNDO/2 sequence as follows (*cf.* Table I): pe band 1, 3e; shoulder 2, $3a_1$; multicomponent band 3, 2e plus one of the Jahn–Teller split 1e; and band 4, the other 1e and $2a_2$. Obviously, there is no direct confirmation, but the vibrational fine structure on the low energy flank of the second pe band (Figure 1, shoulder 2) with $\tilde{\nu} \sim 930$ cm^{-1}, probably due to the a_1 silyl deformation,[8] would not be expected for a degenerate state with numerous overlapping fine structures. The 0.8 eV Jahn–Teller split observed for monosilylacetylene (Table I) lends some credit to the assumed 1e splitting. The remaining two bands at 18.2 and 19.0 eV are fitted into the above CNDO/2 sequence as $2a_1$ and $1a_2$.

The pe spectrum of dimethylacetylene (Figure 1) shows altogether only three separated bands. According to modified CNDO/2 calculations, the components 2–5 (Table I) of the second pe mountain

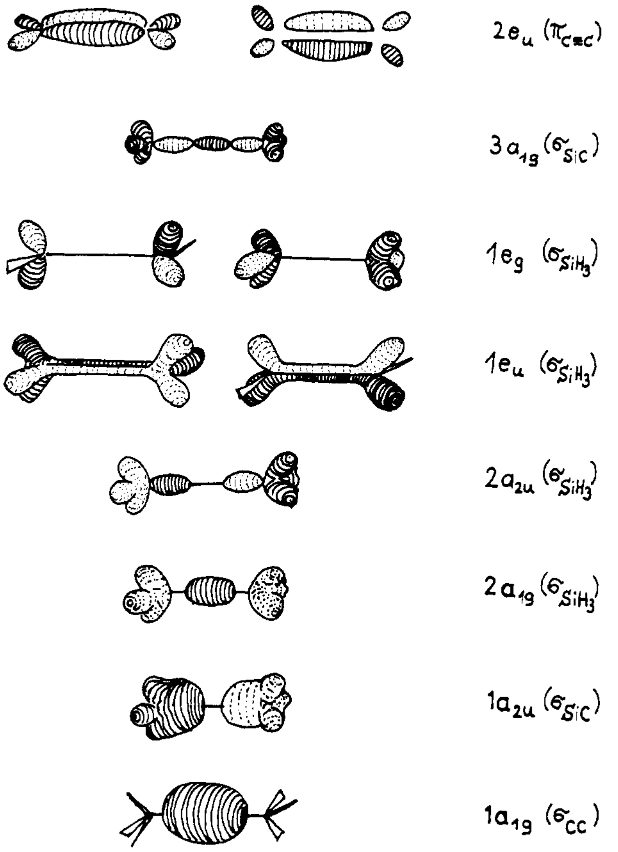

Figure 4. Diagrams showing main bond contributions to the occupied orbitals of disilylacetylene (according to modified CNDO/2 calculations for D_{3d} conformation).

stretching from 13.5 to 16.5 eV are in the same sequence, $3a_1 < 2e < 1e < 2a_2$, as in the disilyl derivative. Vibrational fine structures occur only in the first band ($3e(\pi)$: ground state, 2313 cm^{-1};[15] ion, 2050 cm^{-1}) and in the third band at 20.63 eV ($2a_1$(?): ground state, $\nu_3^{CH_3}(a_1)$ = 1379 cm^{-1};[15] ion, 1090 cm^{-1}). Thus the hyperconjugation model proposed for dimethylacetylene is in agreement with the correct prediction of the π band.

Calculations with or without π Interaction and Silicon 3d Basis Orbitals

In a simple LCBO MO hyperconjugation model, which uses only occupied orbitals as a basis, the interaction parameters β_π^{LCBO} absorb the overall interaction, which cannot be subdivided any further on the basis of the available experimental data. To gain some insight into the interplay of those formal effects, *i.e.*, inductive and/or hyperconjugative destabilization *vs.* stabilizing back-bonding, LCAO MO calculations with and without π interactions and silicon 3d orbitals in the basis set have been performed.

For the calculations a modified CNDO/2 version (see Experimental Section) has been used, which in contrast to conventional CNDO/2 reproduces the pe spectroscopically deduced orbital sequences in both alkyl- and silylacetylenes, mainly due to the reduced π overlap the modified CNDO/2 readjusts, *e.g.*, the order $\pi(3e) < \sigma(3a_1)$ as observed experimentally. The calculations without any π interactions were achieved

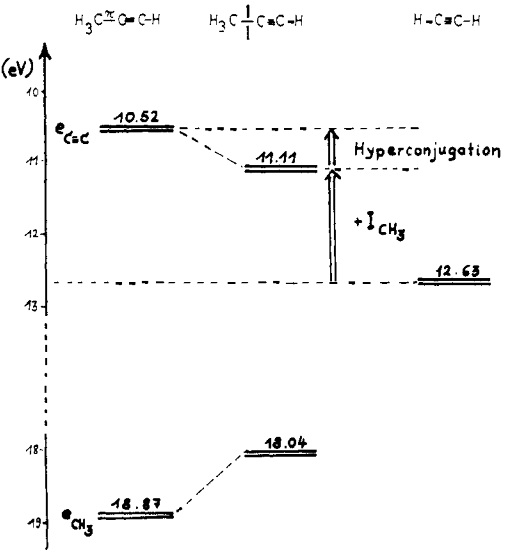

Figure 5. Modified CNDO/2 eigenvalues for the π orbitals o methylacetylene with or without π interaction.

by setting the off-diagonal elements between $\pi_{C\equiv C}$ and π_{XH_3} in the Hartree–Fock matrix equal to zero before diagonalization. The resulting "group orbital" energy $\pi_{C\equiv C}(H_3XC\equiv C–)$, when compared with the calculated π orbital energy of acetylene, reflects the inductive effect of the XH_3 substituent. The procedure is illustrated in Figure 5 for methylacetylene. Within the above approximation the hyperconjugative destabilization of the acetylene π-orbital by a methyl group is smaller than the inductive one. In dimethylacetylene, hyperconjugation contributes 1 eV to the orbital shift and the inductive effect about 1.7 eV, the methyl group perturbations being by far not additive.

For silylacetylene two sets of calculations were carried out, without and with inclusion of silicon 3d orbitals (Figure 6). Comparison within each of the two sets reveals: Only the calculations with the reduced basis ($E_{\text{total}} = -327.2$ eV) yield inductive as well as hyperconjugative π destabilization by the silyl group, both being smaller than the methyl group effects (Figure 5). Inclusion of the silicon 3d orbitals in the basis lowers the total energy as expected ($E_{\text{total}} = -334.7$ eV) but leads to a "negative" hyperconjugative split 3.20 → 3.05 eV (Figure 6), shifting the $\pi_{C\equiv C}$ orbital to higher values $|\epsilon_i|$ than in acetylene itself. This is contrary to the pe data (Table I), which clearly demonstrate, that the acetylene π ionization potential is lowered on silyl substitution. The reason for the exaggerate $p_\pi d_\pi$ back-bonding is traced back to unrealistic overlap relations

$$H_3C\overset{1.46\ \text{Å}}{\text{———}}C(\equiv CH) \qquad H_3Si\overset{1.83\ \text{Å}}{\text{———}}C(\equiv CH)$$

$$S(p_\pi p_\pi) = 0.13 \qquad S(p_\pi p_\pi) = 0.12$$

$$S(p_\pi d_\pi) = 0.18$$

The much too high overlap $S(p_\pi d_\pi)$ leads to a Hartree–Fock off-diagonal element of 2.6 eV compared to a $p_\pi p_\pi$ interaction of only 1.7 eV. As expected from the overlap disproportion, the CNDO/2 calculations with inclusion of $3d_{Si}$ orbitals also fail for disilylacetylene, while those with the reduced $3s_{Si}/3p_{Si}$ basis set allow comparison with other acetylenes as well as with the pe data. Analogous comments were first published by

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(15) *Cf.* G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 2, Van Nostrand, New York, N. Y., 1945, p 356.

Pitt,[16] who recently, in an extensive examination[4] of available experimental data, concluded that numerous ground-state properties of group IV compounds are reasonably reproduced by CNDO/2 calculations with sp basis set. This statement is further confirmed by the calculated charge distributions and dipole moments of methyl- and silylacetylenes. Convincingly, trends and magnitudes of the experimental gas-phase dipole moments[17] are only reflected in modified CNDO/2 calculations without silicon 3d orbitals.

			without	with $3d_{Si}$
H H H	3(+0.038)	H H H	3(−0.074)	3(−0.100)
C	−0.008	Si	+0.405	+0.416
C	−0.023	C	−0.169	−0.197
C	−0.182	C	−0.086	+0.009
H	+0.098	H	+0.070	+0.072
μ^{calcd}	1.013 D		0.135 D	1.536 D
μ^{exptl}	0.781 D[17]		0.316 D[17]	

Concluding Remarks

The preceding discussions of methyl- and silylacetylenes and especially their pe spectra have demonstrated: (i) how simple LCBO MO hyperconjugation models can be parameterized using pe data and how well they predict ionization potentials of related compounds, (ii) why LCAO MO calculations using modified CNDO/2 exaggerate $p_\pi d_\pi$ back-bonding, and (iii) that a basis set without silicon d orbitals better reproduces the dipole moment of silylacetylene and only allows comparison of pe ionization potentials and CNDO/2 eigenvalues within the series RC≡CR (R = H, CH_3, SiH_3).

The main concern for the chemist might be not so much whether $3d_{Si}$ participation is real and provable or not but rather which model will be most useful and easily applicable to rationalize experimental data. Our example shows, that the different lowering of the acetylene π ionization potentials by methyl and silyl groups can be explained by both LCAO MO and LCBO MO models without explicit introduction of $p_\pi d_\pi$ back-bonding. No decision can be made, however, on how much of it might be absorbed in the parameterization—especially within an LCBO MO hyperconjugation approach, which only considers occupied orbitals.

Cradock, Ebsworth, and Whiteford,[10] who published first the pe spectra of most of the silyl and germyl derivatives, $E(XH_3)_n$, of group V to VII elements E, based their assignments mainly on orbital symmetry considerations. Cautiously they pointed out, that the following observations might be in accord with d orbital participation:[10] (i) the first ionization potentials of compounds $E(XH_3)_n$ always reach their maximum value in the silyl derivative $IP_{CH_3} < IP_{SiH_3} > IP_{GeH_3}$, (ii) spin–orbit coupling of heavy atoms is reduced in the silyl relative to the methyl derivative, and (iii) pe bands assigned to electron pair ionizations are usually broadened in the spectra of silyl compounds. These findings could be rationalized within an LCBO MO model as follows. (i) The maximum ionization potential $IP_{CH_3} < IP_{SiH_3} > IP_{GeH_3}$ needs two opposing effects for its explanation, *e.g.*, different inductive electron donation and counteracting $p_\pi d_\pi$ back-bonding in the sequence CH_3-SiH_3-GeH_3. Within the hyperconjugation model, analogous second-order perturbation arguments can be employed; the change in orbital energies is proportional to the square of the interaction term β^2 and thus depends on overlap respectively on bond lengths and inversely proportional to the energy difference between the coulomb parameters $\Delta\alpha$ and thus depends on the relative position of the basis orbitals. Therefore, depending on both the parameters, α and β, a minimum eigenvalue ϵ_i, *i.e.*, *via* Koopmans' theorem $-\epsilon_i \equiv IP_n$, a maximum first-ionization potential can be reproduced. (ii) To incorporate second-order spin-orbit coupling qualitatively into an LCBO MO model,[18] symmetry double groups[19] prove to be useful. For a C_{3v} molecule as silyl iodide,[10] H_3SiI, on inclusion of spin functions in the C_{3v}' double group, only two irreducible representations result, $e_{3/2}$ and $e_{1/2}$. Symmetry allowed mixing yields

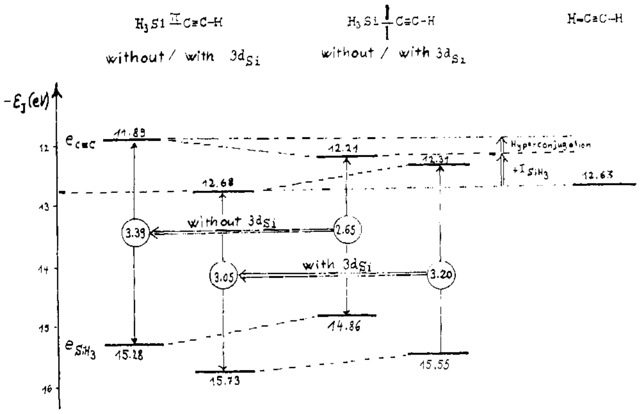
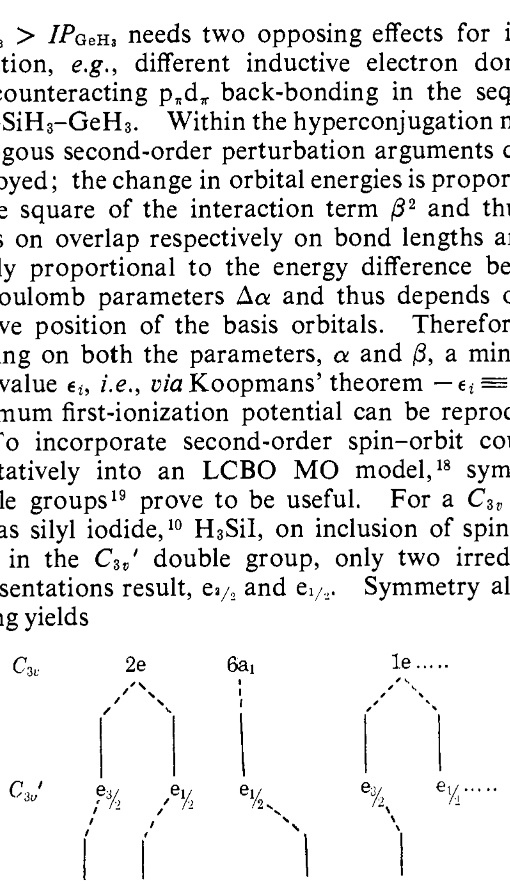


Figure 6. Modified CNDO/2 eigenvalues for the π-orbitals of silylacetylene with and without π overlap and silicon 3d orbitals.



Obviously, the splitting between the adjacent $e_{1/2}$ orbitals must exceed that between the more distant $e_{3/2}$ ones. Thus for silyl iodide a smaller gap between the first two pe bands is expected than for methyl iodide, judging along from second-order spin-orbit coupling. (iii) Also the reasoning for the observed broadening[6] of the first pe bands of silyl compounds[10] does not necessarily have to rest on $p_\pi d_\pi$ delocalization. Within an LCBO MO model it is as easily explained by the stronger mixing of two symmetry equivalent orbitals as their energy distance $\Delta\alpha$ shortens.

Repeatedly it has been pointed out that there is no chance to subdivide LCBO MO parameters unequivocally any further on the basis of experimental data.

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(16) C. G. Pitt, *Chem. Commun.*, 816 (1971); *J. Organometal. Chem.*, 23, C 35 (1970).

(17) R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moments," National Bureau of Standards NSRDS-NBS, 1967, p 10.

(18) K. Wittel, H. Bock, and R. Manne, *Tetrahedron*, in press; K. Wittel, *Chem. Phys. Lett.*, 15, 555 (1972).

(19) *Cf.* for instance G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand, New York, N. Y., 1966, p 563.

Therefore the hyperconjugation model, well suited to help in assigning the pe spectra of alkyl- and silylacetylenes, does neither prove nor disprove $p_\pi d_\pi$ backbonding in silicon compounds—just as most of the numerous arguments produced favor one or the other.

Experimental Section

Synthesis. Monosilylacetylene[20] was prepared from acetylene magnesium bromide and iodosilane in dry, degased tetrahydrofuran. The reaction product was pumped off and purified by fractionate condensation. The measurement sample was finally obtained by high vacuum line distillation between two baths at −112 and −132° and its purity controlled by ir[21] and nmr[20] as well as molecular weight determination (found 56.8, calcd 56.1).

Disilylacetylene[22] can be obtained analogously from acetylene di-Grignard solution in dibutyl ether and bromosilane. The measurement sample was purified from dibutyl ether by fractionate condensation at −78 and at −96° from excess bromosilane. Neither by ir and nmr nor by molecular weight determination (found 87.0, calcd 86.2) could any impurities in the measurement sample be detected.

Spectra. The pe spectrum of methylacetylene was taken from the literature;[7] the one of dimethylacetylene has been kindly given to us by Elbel[23] from our group. The pe spectra of the silylacetylenes were recorded with a Perkin-Elmer PS 16 and calibrated with argon. The samples have been introduced into the spectrometer carefully avoiding exposition to air.

Calculations. The calculations have been carried out at the UNIVAC 1108 of the computer center of the University of Frankfurt. The modified CNDO/2 version used is described elsewhere.[24] In addition the $\beta_A{}^0$ values for the third-period elements have been reduced proportionally to $\beta_{\text{carbon}}{}^0$.[24] The π interaction was switched off by setting the corresponding *A*(*i,j*) in subroutine SCFCLO equal to zero. Silicon d orbitals can be excluded by either reducing the basis set or by setting all d overlap integrals in subroutine INTEGRL equal to zero. The latter procedure allows alternatively a reduction of the back-bonding by multiplying the d overlap integrals with a factor <1.

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(20) E. A. V. Ebsworth and S. G. Frankiss, *J. Chem. Soc.*, 661 (1963).

(21) E. A. V. Ebsworth, S. G. Frankiss, and W. J. Jones, *J. Mol. Spectrosc.*, **13**, 9 (1964); R. B. Reeves, R. E. Wilde, and D. W. Robinson, *J. Chem. Phys.*, **40**, 125 (1964).

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Triarylphosphine, Hydride, and Ethylene Complexes of Rhodium(I) Chloride

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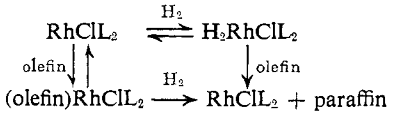
Abstract: Physical studies, combining molecular weights, ^{31}P, ^{13}C, and ^1H nmr, infrared, and spectrophotometric measurements, have been made to define the species and rates and equilibria of reactions in solutions containing mixtures of Rh^ICl, triarylphosphines [PPh_3 or $P(p\text{-tolyl})_3$], H_2, ethylene, and cyclohexene. The $RhClL_3$ complexes do not dissociate to $RhClL_2$ to a spectroscopically detectable extent but are in equilibrium with the chlorine bridged dimer $[RhClL_2]_2$. The dimer reacts with H_2 to form $H_2[RhClL_2]_2$ and is readily cleaved by L or ethylene, but not cyclohexene, to form $RhClL_3$ or $(C_2H_4)RhClL_2$. The dimer itself is a good homogeneous hydrogenation catalyst. A species of composition $RhClL_2$, while not spectroscopically detectable, must be postulated as a kinetic intermediate in order to explain the kinetics of H_2 reaction with solutions of $RhClL_3$ or of H_2 with cyclohexene in solutions of $[RhClL_2]_2$.

In 1966 Wilkinson and coworkers reported the rapid homogeneous hydrogenation of olefins catalyzed by $RhCl(PPh_3)_3$.[2] They proposed a mechanism shown in Scheme I. Complete dissociation of $RhCl(PPh_3)_3$ into $RhCl(PPh_3)_2$ and PPh_3 was suggested on the basis of an experimental molecular weight about half the theoretical value. $(C_2H_4)RhCl(PPh_3)_2$ and a compound thought to be $H_2RhCl(PPh_3)_2$ were isolated from the reactions of $RhCl(PPh_3)_3$ with C_2H_4 and H_2. A rather insoluble compound with the composition of $[RhCl(PPh_3)_2]_2$ could be precipitated from solution on standing or heating. The solubility increased under H_2; volume uptake and molecular weight measurements suggested a binuclear tetrahydride.

Scheme I



Several subsequent studies have appeared.[3] A preliminary X-ray crystal structure of $RhCl(PPh_3)_3$ has been reported.[4] Molecular weight[5] and ^{31}P nmr studies[6,7] have established that the complex remains largely intact in relatively concentrated solutions. Uv studies[8] with L = PPh_3 have been interpreted in terms

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