Journal of Organometallic Chemistry, 251 (1983) 7–14
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

σ-BOND CONJUGATION IN POLYSILANES, A PES SCALED FREE-ELECTRON APPROACH FOR THE INTERPRETATION OF SKELETAL CLEAVAGE REACTIONS

ALEKSANDER HERMAN, BOGUSŁAW DRĘCZEWSKI and WIESŁAW WOJNOWSKI

Institute of Inorganic Chemistry and Technology, Technical University, 80–952 Gdańsk (Poland)

(Received November 18th, 1982)

Summary

The σ-orbital energies calculated by the simple free-electron model with a parametrization procedure proposed recently by Von Szentpaly correlate very closely with the σ-band positions of the corresponding photoelectron spectra. For the σ-orbitals of three series of molecules: $H(CH_2)_nH$ ($n = 2$–4); $H(SiH_2)_nH$ ($n = 2$–5); $Me(SiMe_2)_nMe$ ($n = 2$–4) the FEMO model yields a standard error (SE) of 0.060 eV. Compared with HMO results (LCGO, LCBO and Sandorfy C) the correlation is significantly improved. The free-electron results are more accurate than those obtained using the PPP, CNDO/2, MINDO/3, SAMO and ab initio methods.

The free-electron frontier orbital densities were successfully used to account for features of the skeletal cleavage reactions of polysilanes.

The conjugative properties of carbon π-electron systems have been successfully interpretated by the free-electron molecular orbital models (FEMO) [1]. Recently Von Szentpaly worked out a method for interpretation of photoelectron spectra of aromatic hydrocarbons based on FEMO, which gives the best input-to-output ratio for calculation of the π-band positions [2]. In his latest work Von Szentpaly successfully calculated the partial rate factors for electrophilic aromatic substitution reactions based on the same model [3].

It is known that ionization potentials and electronic spectra of the C, Si, Ge and Sn catenates are qualitatively similar and reflect some general conjugative properties of σ-systems [4]. Thus,Von Szentpaly's procedure [2] might also be applicable to calculation of the σ-band positions of the linear catenated σ-systems of carbon and silicon. We expected that this simple PES scaled free-electron approach would lead to an interpretation of consecutive skeletal cleavage reactions, e.g. halogenation of permethylpolysilanes [5,6].

Results and discussion

Ionization potentials

The calculations were carried out with the following assumptions:

0022-328X/83/$03.00

(1) in a molecule $R(R_2M)_nR$, only the M–M σ-bond molecular orbitals are considered;

(2) the electrons are treated as electrons in one-dimensional potential well of a length $L = nD$ and a depth U. D is the average M–M bond distance;

(3) the introduced effective electron mass $m^\star$ is responsible for the M–R tails and electron-nucleus interactions;

(4) $m^\star/m$ and U are treated as scaling factors in order to reproduce the absolute separation of the energy levels.

$$\mathrm{VIP}_j^0 = -\varepsilon_j = U - \left(\hbar^2 k_j^2/2m^\star\right) \tag{1}$$

Thus, the number of adjustable parameters is the same as in the HMO model. The regressional problem [2] is the same as in HMO method, and can be solved by standard least-squares techniques. In eq. 1, $k_j = 2\pi/\lambda_j$ and $\lambda_j = 2L/n_j$; λ_j is the De Broglie wavelength of the j-th free-electron orbital.

Table 1 presents the calculated and observed [4] values of Vertical Ionization Energies for alkanes (M = C, R = H and D 1.54 Å), polysilanes (M = Si, R = H and D 2.34 Å) and permethylpolysilanes (M = Si, R = Me and D 2.34 Å).

The parameters of the regression lines which were obtained for three series of molecules listed in Table 1 are summarized in Table 2. For comparison the corresponding parameters for π-orbitals of aromatic hydrocarbons [2] are also included.

The differences between U values for series with M = C and M = Si may be rationalized by comparison with the valence state ionization energy of carbon and silicon atoms [7]. The same interpretation probably applies to the difference between U values for σ-systems of aliphatic hydrocarbons and π-systems of aromatic hydrocarbons.

For the series with the same M (M = Si), the U value depends on ionization energy of R. The striking difference between the $m^\star$ values for σ and π systems of hydrocarbons should be emphasized. The $m^\star$ values depend strongly on M, but only slightly on R.

Figure 1 shows the correlation of the ionization energies calculated by FEMO with the observed VIP_j values. The FEMO-correlations for σ-systems are significantly better than that for the π-system [2]. The standard error for linear σ-systems is 0.060 eV, that is, it less than the experimental uncertainty, which is up to 0.10 eV [8]. The FEMO results are comparable with those obtained by other models. The standard errors are summarized in Table 3. Only variance minimization by adjusting two additional parameters without physical significance, according to eq. 2 gives

$$\mathrm{VIP}_j^0 = A + B\varepsilon_j \tag{2}$$

results which are comparable to those obtained from FEMO. Compared with HMO results (LCGO, LCBO and Sandorfy C), the correlation is significantly improved. The free-electron results are more accurate than those obtained by the PPP, CNDO/2, MINDO/3, SAMO, and ab initio methods.

The frontier-orbital density and skeletal cleavage

According to our calculations the FEMO model leads to charge distributions similar to those from HMO models. There is little experimental information which

TABLE 1

COMPARISON OF CALCULATED AND OBSERVED VERTICAL IONIZATION ENERGIES (VIP) [4] (ALL VIP VALUES IN eV)

Molecule	Orbital	k_j^2 (Å^{-2}) FEMO	VIP$_j$obs	$\mathrm{VIP}^0_{j\mathrm{FEMO}}$	$\mathrm{VIP}^{\mathrm{HMO}}_{j\mathrm{LCGO}}$ [a]	$\Delta\mathrm{VIP}^0_{j\mathrm{FEMO}}$ [b]	$\Delta\mathrm{VIP}^{\mathrm{HMO}}_{j\mathrm{LCGO}}$ [c]
$H(CH_2)_nH$							
$n = 2$	g	1.040	12.10	12.10	12.10	0.0_0	0.0_0
$n = 3$	u	1.850	11.40	11.39	11.39	0.0_1	0.0_1
$n = 4$	g	2.341	10.95	10.96	10.95	−0.01	0.00
$H(SiH_2)_nH$							
$n = 2$	g	0.451	10.53	10.37	10.51	0.16	0.02
$n = 3$	u	0.801	9.87	9.88	9.96	−0.01	−0.09
	g	0.200	10.72	10.72	10.74	0.00	−0.02
$n = 4$	g	1.014	9.62	9.59	9.61	0.03	0.01
	u	0.451	10.32	10.37	10.30	−0.05	0.02
	g	0.113	10.85	10.84	10.85	0.01	0.00
$n = 5$	u	1.154	9.36	9.39	9.40	−0.03	−0.04
	g	0.649	10.06	10.09	9.96	−0.03	0.10
	u	0.288	10.56	10.60	10.51	−0.04	0.05
	g	0.0721	10.86	10.90	10.91	−0.04	−0.05
$Me(SiMe_2)_nMe$							
$n = 2$	g	0.451	8.69	8.76	8.87	−0.06	−0.18
$n = 3$	u	0.801	8.19	8.24	8.28	−0.05	−0.09
	g	0.200	9.14	9.13	9.11	0.01	0.03
$n = 4$	g	1.014	7.98	7.92	7.92	0.06	0.06
	u	0.451	8.76	8.76	8.64	0.00	0.12
	g	0.113	9.30	9.26	9.23	0.04	0.07

[a] Linear Combination Group Orbitals [10]. [b] $\Delta\mathrm{VIP}^0_{j\mathrm{FEMO}} = \mathrm{VIP}_{j\,\mathrm{obs}} - \mathrm{VIP}^0_{j\mathrm{FEMO}}$. [c] $\Delta\mathrm{VIP}^{\mathrm{HMO}}_{j\mathrm{LCGO}} = \mathrm{VIP}_{j\,\mathrm{obs}} - \mathrm{VIP}^{\mathrm{HOMO}}_{j\mathrm{LCGO}}$.

TABLE 2

THE PARAMETERS OF THE REGRESSION LINES FOR THE SERIES OF MOLECULES LISTED IN TABLE 1

Molecule	U (eV)	$\hbar^2/2m^*$ (eV Å^2)	$m^*(m)$
$H(CH_2)_nH$	13.021 ± 0.025	0.882 ± 0.014	4.320
$H(SiH_2)_nH$	10.997 ± 0.037	1.390 ± 0.058	2.741
$Me(SiMe_2)_nMe$	9.426 ± 0.042	1.484 ± 0.071	2.566
Aromatic hydrocarbons [2]	12.209 ± 0.072	5.135 ± 0.111	0.740

can be used to test the predictions. Some information about electron densities in silicon chains may be obtained from skeletal cleavage studies of polysilanes, but the available experimental data for the cleavage of permethylpolysilanes [4–6] are only qualitative.

In order to test our results, we obtained kinetic data for the reactions of 1,4-$Cl_2Si_4Me_8$ and Si_6Me_{12} with chlorine (Fig. 3a and 4a). The kinetic data for the investigated consecutive reactions (Fig. 3 and 4), and some computer simulated curves (Fig. 3b and 4b) are shown. The simulated curves were calculated on the assumption that all the partial rate factors have the same value. Comparison of the figures shows that the experimental and calculated results are quite different, which means that there are large differences between the partial rate factors, particularly for 1,4-$Cl_2Si_4Me_8$ (Fig. 3). Figure 2 shows the frontier-orbital densities (FOD) in the silicon chain of linear polysilanes with non-equivalent Si–Si bonds as calculated

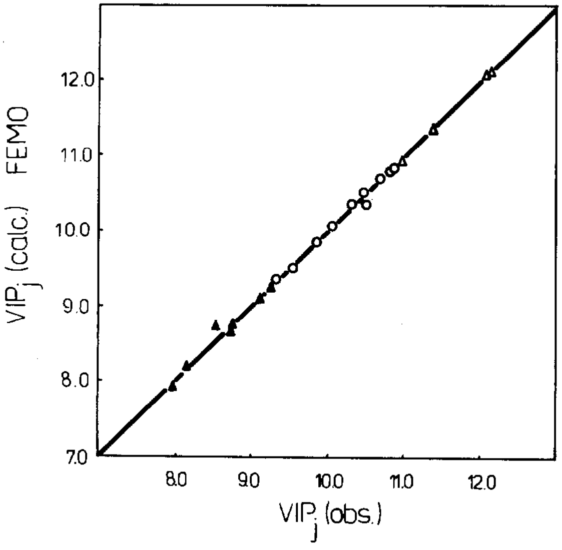


Fig. 1. Correlation of FEMO ionization energies with the observed vertical ionization energies in eV; △-$H(CH_2)_nH$; O-$H(SiH_2)_nH$; ▲-$Me(SiMe_2)_nMe$.

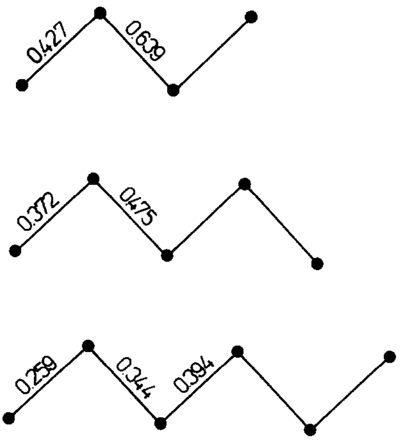


Fig. 2. Frontier-orbital densities (FOD) of linear polysilanes with non-equivalent Si–Si bonds calculated using FEMO model.

TABLE 3

STANDARD ERRORS (*SE*) (VIP) FOR THE VARIOUS MODELS

Model	Reference	*SE* (VIP) (eV)			
		$H(CH_2)_nH$	$H(SiH_2)_nH$	$Me(SiMe_2)_nMe$	average
FEMO	[2] [a]	0.013	0.066	0.055	0.060
LCGO	[10] [a]	0.009	0.058	0.125	0.083
HMO LCBO	[11] [a]	0.090	0.129	0.050	0.108
Sandorfy C	[12] [a,b]	0.077	0.135	0.044	0.111
scaled MINDO/3	[13,14]	0.107	0.106	–	0.156
scaled CNDO/2	[15] [a]	0.102	0.115	–	0.196
MINDO/3	[13,14]	0.382	0.193	–	0.212
scaled CNDO/2	[16]	–	0.212	–	0.212
SCF MO	[17]	0.708	–	–	0.708
PPP	[18]	1.157	–	–	1.157
SAMO	[19]	1.686	–	–	1.686
ab initio	[19]	1.984	–	–	1.984
CNDO/2	[16]	–	2.825	–	2.825
CNDO/2	[15] [a]	5.138	3.723	–	3.871

[a] VIP_j^0 calculated in this paper. [b] $\beta_{gem}/\beta = 0.35$ for C and 0.38 for Si.

by the FEMO model. The results of FOD calculated by other MO models are reported in Table 4.

$1,4\text{-}Cl_2Si_4Me_8$ is the smallest catenate with non-equivalent Si–Si bonds. From Fig. 3 it can be seen that the cleavage of $1,4\text{-}Cl_2Si_4Me_8$ occurs preferentially at the

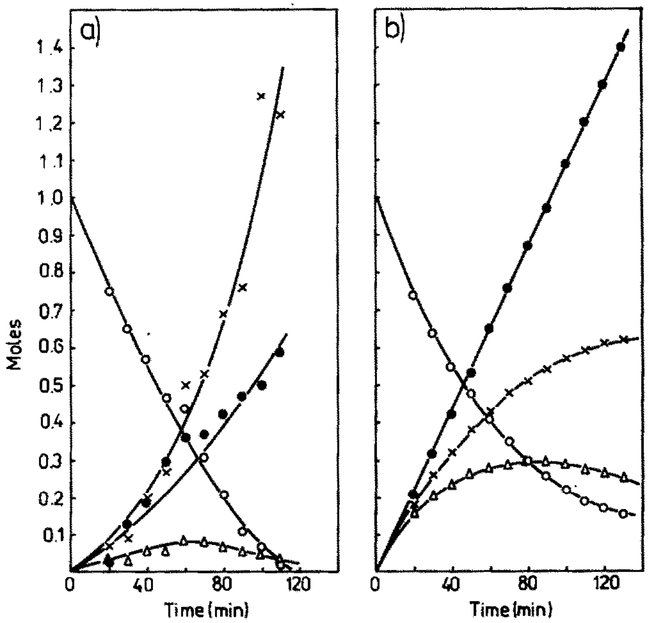
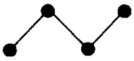
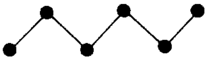


Fig. 3. The course of the reaction of $1,4\text{-}Cl_2Si_4Me_8$ with chlorine: (a) experimental and (b) theoretical; ○-$1,4\text{-}Cl_2Si_4Me_8$; △-$1,3\text{-}Cl_2Si_3Me_6$; ×-$1,2\text{-}Cl_2Si_2Me_4$; ●-$1,1\text{-}Cl_2SiMe_2$.

TABLE 4

FRONTIER-ORBITAL DENSITIES (FOD) OF POLYSILANES CALCULATED USING DIFFERENT MO MODELS

Polysilane	Position	FOD		
		FEMO [2]	LCBO [7]	Sandorfy C [8]
	1-2	0.427	0.500	0.261
	2-3	0.639	1.000	0.457
	1-2	0.372	0.277	0.153
	2-3	0.475	0.725	0.336
	1-2	0.259	0.167	0.097
	2-3	0.344	0.500	0.240
	3-4	0.394	0.666	0.319

central σ-bond. It can also be seen from Fig. 4 that cleavage of 1,6-$Cl_2Si_6Me_{12}$ occurs preferentially at the central Si–Si σ-bonds. If skeletal cleavage by chlorine is predominantly frontier-orbital controlled the cleavage of the central Si–Si bonds would be predicted by the simple FEMO model (Fig. 2). This suggests that the first step of the chlorine cleavage of polysilanes is a one electron-transfer process from

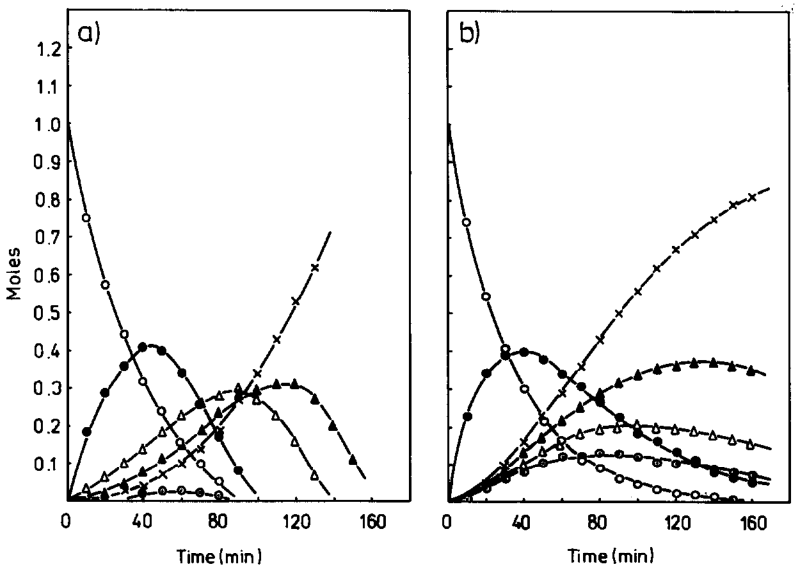


Fig. 4. The course of the reaction of Si_6Me_{12} with chlorine: (a) experimental and (b) theoretical; ○-Si_6Me_{12}; ●-1,6-$Cl_2Si_6Me_{10}$; ⊙-1,5-$Cl_2Si_5Me_{10}$; △-1,4-$Cl_2Si_4Me_8$; ▲-1,3-$Cl_2Si_3Me_6$; ×-1,2-$Cl_2Si_2Me_4$.

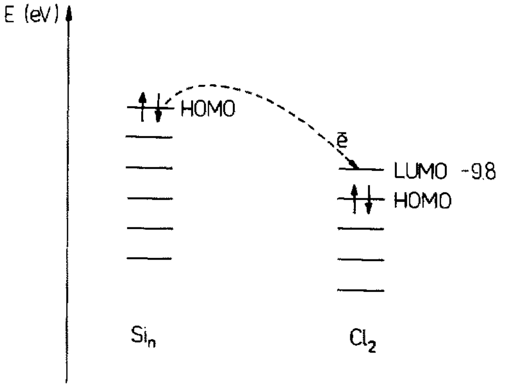


Fig. 5. Electron transfer process between polysilane and chlorine initiated the cleavage reaction.

HOMO of polysilanes to LUMO of chlorine molecule. The comparison of HOMO energy values of polysilanes (Table 1) with the LUMO energy of the chlorine molecule (Fig. 5) strongly supports this suggestion.

Experimental

The kinetic data for the chlorination of permethylpolysilanes were obtained by GC (4 mm OD 3-meter steel column, QF-1, 20% on Chromosorb W-NAW, 60–80 mesh, helium flow 50 ml min^{-1}). A thermal conductivity detector was used. Chlorine was passed into the reaction vessel after 1/4 dilution with argon. The flow rate was 50 ml min^{-1}.

Dodecamethylcyclohexasilane was prepared as described by West and Wojnowski [9], and 1,4-$Cl_2Si_4Me_8$ was obtained by chlorination of Si_6Me_{12} [6].

The details of the computer programs for the simulations of the pattern of the consecutive reactions will be supplied on request to the authors.

The chlorination of Si_6Me_{12}

A 25 ml three-necked flask equipped with capillary inlet tube, reflux condenser and syringe septum was charged with 20 ml CCl_4 and 4 g Si_6Me_{12}. The flask was cooled with an ice bath and the flow of chlorine initiated, rapid magnetic stirring being maintained throughout the reaction. Every 10 min a one μl sample of the reaction mixture was withdrawn via septum with a syringe and analyzed by GC. The reaction was stopped at the point at which only 1,2-$Cl_2Si_2Me_4$ remained. The results of this reaction are shown graphically in Fig. 4a.

The chlorination of 1,4-$Cl_2Si_4Me_8$

1,4-$Cl_2Si_4Me_8$ was chlorinated in the same way. 10 ml of 1,4-$Cl_2Si_4Me_8$ without solvent was placed in a 25 ml flask and chlorine was bubbled through. Every 10 min, a one μl sample of the reaction mixture was withdrawn and analyzed by GC. The reaction was continued untill all the 1,4-$Cl_2Si_4Me_8$ had undergone chlorination. The results are shown in Fig. 3a.

Acknowledgement

The authors are grateful to the Polish Academy of Sciences (problem MR I 12) for financial support of this research.

References

1 J.R. Platt, K. Ruedenberg, C.W. Scherr, N.S. Ham, H. Labhart and W. Lichten, Free-electron theory of conjugated molecules: A source book, Wiley, Inc. New York, 1964.
2 L. von Szentpaly, Chem. Phys. Letters, 67 (1979) 63.
3 L. von Szentpaly, Chem. Phys. Letters, 77 (1981) 352.
4 C.G. Pitt in A.L. Rheingold (Ed.), Homoatomic rings, chains and macromolecules of main-group elements, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 1977, p. 203.
5 W. Wojnowski, C.J. Hurt and R. West, J. Organomet. Chem., 124 (1977) 271.
6 C.H. Middlecamp, W. Wojnowski and R. West, J. Organomet. Chem., 140 (1977) 133.
7 J. Hinze and H.H. Jaffe, J. Am. Chem. Soc., 84 (1962) 540.
8 R. Boschi, J.N. Murrell and W. Schmidt, Discussions Faraday Soc., 54 (1972) 116.
9 R. West, L. Brough and W. Wojnowski, Inorg. Syntheses, Vol. XIX, (1979) 356.
10 C.G. Pitt, M.M. Bursey and P.F. Rogerson, J. Am. Chem. Soc., 92 (1970) 519.
11 E. Heilbronner and H. Bock, Das HMO-Model und seine Anwendung, Verlag Chemie, GmbH., Weinheim, 1968.
12 C. Sandorfy, Can. J. Chem., 33 (1955) 1337.
13 R.C. Bingham, M.J.S. Dewar and D.H. Lo, J. Am. Chem. Soc., 97 (1975) 1204.
14 M.J.S. Dewar, D.H. Lo and C.A. Ramsden, J. Am. Chem. Soc., 97 (1975) 1311.
15 J.A. Pople and G.A. Segal, J. Chem. Phys., 44 (1966) 3289.
16 H. Bock, W. Ensslin, F. Feher and R. Freund, J. Am. Chem. Soc., 98 (1976) 668.
17 M.J.S. Dewar and G. Klopman, J. Am. Chem. Soc., 89 (1967) 3089.
18 S. Katagiri and C. Sandorfy, Theoret. Chim. Acta, 4 (1966) 203.
19 J.E. Eilers and D.R. Whitman, J. Am. Chem. Soc., 95 (1973) 2067.