

A NEW STERIC PARAMETER, OV. 2. COMPUTING
PRINCIPLES, IMPLEMENTATION, APPLICATIONS

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Content : The previous paper of the series described in the Frame of set theory, a new method to treat quantitatively the steric effects. The method was termed OVA -Overlapping Volume Analysis. The present paper explicitly discusses the computing method, the FORTRAN program which implements the method and some illustrative applications.

1. Introduction

The OVA method (Overlapping Volume Analysis) was developed¹ by one of us in order to account quantitatively for the steric effects in the LFER frame work. The aim of OVA is to avoid the known deficiencies of the Taft - type methods (for a short review in this context, see ref. 2, and for further applications of OVA, ref. 3).

In principle, OVA implies the use of the steric parameter OV in a linear regressional equation. OV signifies the overlapping Van der Waals volume of the reactants in the transition state. Illustratively, consider the transition shown in figure 1. A and B denotes the Van der Waals envelope of the two molecules, reaction coordinate¹³ coincides with the x axis, and the two molecules are r [Å] apart each another. The OV value $[A^3]$ is evidenced by the shadowed area.

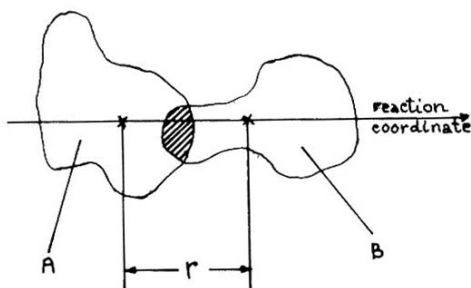


FIG. 1

2. OVA - Computing Principles

Consider two chemically reactive species (molecules, ions, radicals etc.), having N_1 and N_2 atoms, respectively. From a steric viewpoint, an atom of a given molecule is well characterized by its cartesian coordinate and Van der Waals radius. The Van der Waals anvelopes of the two considered chemical species are assembled by N_1 , respectively N_2 spheres.

We recall, from ref. 1, that OV is given by relation (1) :

$$OV = \alpha |W_2| / |W_1| \quad (1)$$

where α stands for the volume of the parallelepiped which circumscribes the Van der Waals anvelopes of the two considered chemical species. W_2 is the set of the points which lie within the overlapping volume of the two Van der Waals anvelopes, and W_1 is the set of the points within the parallelepiped of volume α (see figure 1). $| |$ denotes the cardinal.

The points $w_1 \in W_1$ and $w_2 \in W_2$ are random points with uniform repartition. W_1 and W_2 are generated by means of the same random numbers generators ; obviously, $W_2 \subset W_1$.

It is clear, relation (1) implies the use of Monte Carlo technique⁴⁻⁶.

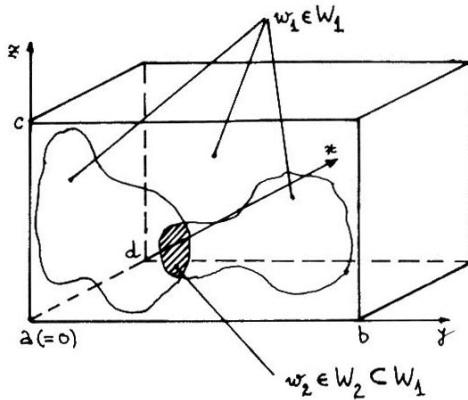


FIG. 2

OVA computations use the Monte Carlo technique as follows :

1) The random numbers $\varphi \in (0, 1)$ are generated using a random numbers generator (in our case, ALEAT, based on Lehmer algorithm⁶). This algorithm implies the following iterative procedure⁴ :

$$m_{k+1} = 5^{17} m_k \pmod{2^{40}}$$

$$\varphi_{k+1} = 2^{-40} m_k$$

m_1 is given. The period of ALEAT is $2^{34} + 1$.

2) Using φ one builds up the set W_1 on desired cardinality in this way : if $(b - a)$, $(d - a)$ and $(c - a)$ are the dimensions of the parallelepiped edges (see fig. 1), the point $w(w_x, w_y, w_z) \in W_1$ is given by

$$w_x = a + (d - a) \varphi_1$$

$$w_y = a + (b - a) \varphi_2$$

$$w_z = a + (c - a) \varphi_3$$

$\varphi_1, \varphi_2, \varphi_3$ being any three consecutive random numbers

$\xi \in (0, 1)$

3) The set W_2 is obtained by selecting those $w(w_x, w_y, w_z) \in W_1$ which satisfy one of the systems of inequations (3) :

$$\begin{cases} (X_{1J} - w_x)^2 + (Y_{1J} - w_y)^2 + (Z_{1J} - w_z)^2 < R_{1J}^2 \\ J = 1, 2, \dots, N_1 \\ (X_{2I} - w_x)^2 + (Y_{2I} - w_y)^2 + (Z_{2I} - w_z)^2 < R_{2I}^2 \\ I = 1, 2, \dots, N_2 \end{cases} \quad (2)$$

4) $\alpha = (b-a)(d-a)(c-a)$, and OV is computed according to relation (1).

It is well known⁴, the error in Monte Carlo computations is proportional to $(D/|W_1|)^{1/2}$ where D is a constant. In order to achieve a satisfying accuracy, one needs to use $|W_1| \simeq 10^5$.

3. OVA - Implementation

The OVA computing method, described in the previous section, is easy to implement. Our program has the following features :

Name : STEREO/1
Language : FORTRAN IV
Hardware : IBM, IRIS 50 etc.
Memory : 20 KØ
Source : 180
Computing time : depends on W_1 . For $W_1 = 10^4$
the computing time is about 80
seconds.

The STEREO/2 version of the program (in progress) will allow completely automatized OVA computations.

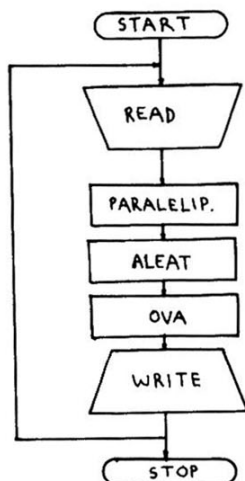


FIG. 3. Flow chart of STEREO/1.

4. OVA - Strategy

Consider the distance denoted by r in figure 4 as reaction coordinate for a considered reaction.

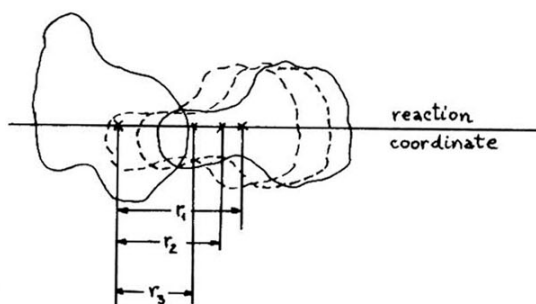


FIG. 4.

Let be a series of N molecules which suffer the same reaction via the same mechanism and measure, for instance,

the reaction rate k_I , $I = 1, 2, \dots, N$.

The steric effects in considered reaction are expressed quantitatively by linear model (1) :

$$\log k_I = a + b OV_I \quad (3)$$

a and b being calculated by the least squares method.

The geometry of transition state and reaction coordinate are approximated from molecular orbital calculations. It is necessary to determine appropriate position of transition state on reaction coordinate, i.e. to determine appropriate value of r in fig. 4. The following strategy is used : one computes $OV_I(r_J)$, $I = 1, 2, \dots, N$, $J = 1, 2, \dots, M$, then the M equations (3) and finally one selects the best equation.

The above procedure can be systemized as follows :

$$\left. \begin{array}{l} OV_1(r_1), OV_2(r_1), \dots, OV_N(r_1) \xrightarrow{\text{eq.3, } R_1} \\ OV_1(r_2), OV_2(r_2), \dots, OV_N(r_2) \xrightarrow{\text{eq.3, } R_2} \\ OV_1(r_M), OV_2(r_M), \dots, OV_N(r_M) \xrightarrow{\text{eq.3, } R_M} \end{array} \right\} \Rightarrow \left. \begin{array}{l} r_K, \\ R_K = \text{MAX}_{J=1}^M (R_J) \end{array} \right\} \quad (4)$$

R_J stands for the regressional coefficient of eq.3 obtained with the $OV_I(r_J)$ values, $I = 1, 2, \dots, N$.

The procedure (4) is justified in the LFER frame because the electronic parameters (σ_H , σ_I , σ_R , \mathcal{F} , \mathcal{R} , etc.), denoted by Σ , verify the equation (5) :

$$\frac{\partial \Sigma}{\partial r} = 0 \quad (5)$$

If an electronic reactivity index which depends on r , $I(r)$, is available, then the model (3) will be changed according to :

$$\log k_I = a + b OV_I(r) + c I_I(r) \quad (6a)$$

or

$$\log k_I = a' + b' I_I(r) \Rightarrow r_K \text{ and then}$$

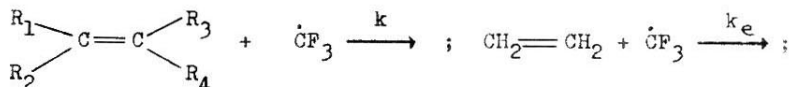
$$\log k_I = m + n OV_I(r_K) + p I_I(r_K) \quad (6b)$$

In the next section of the paper we illustrate the

OVA method using strategy (4) and compare the OVA equation with the Taft - type ones.

5. Applications - The Radical Addition to Alkenes

Consider the reactions :



characterized by the relative rate constants $k_r = k/k_e$. The k_r values were obtained by Vertommen et al⁷ in the gas phase, thus being free of solvent effects (for a recently published review, see ref. 8). The k_r values are collected in table 1.

Table1. The k_r values

No.	Alkene	k_r
1.	$\rightarrow H_2C = CHF$	0,49
2.	$\rightarrow H_2C = CF_2$	0,15
3.	$\rightarrow H_2C = CHCF_3$	0,40
4.	$\rightarrow H_2C = CHCH_3$	2,30
5.	$\rightarrow HFC = CH_2$	0,56
6.	$\rightarrow HFC = CF_2$	0,031
7.	$\rightarrow F_2C = CH_2$	0,0055
8.	$\rightarrow F_2C = CHF$	0,016
9.	$\rightarrow F_2C = CF_2$	0,12
10.	$\rightarrow H(CF_3)C = CH_2$	0,008
11.	$\rightarrow H(CH_3)C = CH_2$	0,20

\rightarrow indicates the site of addition.

In order to verify the importance of the electronic effects, one has computed the correlations $\log k_r$ vs σ_p and $\log k_r$ vs F_C and the correlational coefficients of 0,35 and 0,65, respectively, were obtained.

F_C stands for Swain - Lupton field constant computed according to the equation :

$$\mathcal{F}_C = \mathcal{F}_{R_1} + \mathcal{F}_{R_2} + \frac{1}{3} (\mathcal{F}_{R_3} + \mathcal{F}_{R_4})$$

The E_S - type steric constants and OVA method were used to investigate the importance of steric effects.

5.1. Taft - Type Correlations

The steric constants and \mathcal{F}_C used in correlations are collected in table 2. The values of these constants are taken from our literature compilations^{9, 10}.

Table 2. Parameters used in correlations .

Alkene No.	$\sum v$	$\sum E_S^e$	$\sum MR$	$\sum E_S$	\mathcal{F}_C
1.	0.00	0.00	2.00	2.48	0.236
2.	0.00	0.00	2.00	2.48	0.472
3.	0.00	0.00	2.00	2.48	2.210
4.	0.00	0.00	2.00	2.48	-0.017
5.	0.27	-0.46	1.80	1.73	0.708
6.	0.27	-0.46	1.80	1.73	1.180
7.	0.54	-0.92	1.60	0.98	1.416
8.	0.54	-0.92	1.60	0.98	1.652
9.	0.54	-0.92	1.60	0.98	1.888
10.	0.91	-2.40	6.00	0.08	0.631
11.	0.52	-1.24	6.70	1.24	0.052

\sum is taken over the substituents of the site of addition.

MR expresses the Van der Waals volume, WV, of the substituent, as was pointed out¹¹ by one of us :

$$MR = -2.678 + 0.337 WV \quad (7)$$

n	r	s	F	EV
20	0.95	1.50	76.83	0.94

where n - the number of points used in correlation

r - correlation coefficient

s - standard deviation

F - Fischer statistics, EV - explained variance.

MR was used in order to check the vectorial character of the steric effects. The very low correlation (8) argues that the steric effects in here considered reactions are vectorial :

$$\log k_r = -0.785 - 0.007 \sum MR \quad (8)$$

n	r	s	F	EV
11	0.15	0.83	0.1	0.08

The other obtained equations are :

$$\log k_r = -0.304 - 2.049 \sum v \quad (9)$$

n	r	s	F	EV
11	0.75	0.55	5.17	0.52

$$\log k_r = -2.238 + 0.789 \sum E_S \quad (10)$$

n	r	s	F	EV
11	0.77	0.54	5.83	0.55

$$\log k_r = -0.459 + 0.773 \sum E_S^e \quad (11)$$

n	r	s	F	EV
11	0.68	0.62	3.36	0.40

Eqs. (9) - (11) evidence the retarding effect of bulkier substituents. The correlations are rather poor (but significant according to F because both steric and electronic factors condition k_r).

5.2. OVA Computations

The OVA computations were performed considering the transition state shown in figure 5 (i.e. π - type overlapping ; the σ - type overlapping was not tested).

The values of Van der Waals radii of the atoms used in computations are taken from ref. (12) : H(1.24 Å), C(1.57 Å), F(1.35 Å). Standard bond lengths and angles were considered. The OV figures were computed by means of 60.000 random numbers.

The following correlation coefficients are obtained for eq. (12) :

$$\log k_r = a + bOV(r) \quad (12)$$

r	4.0	3.8	3.4	3.2	3.0
regressional coefficient	0.40	0.45	0.51	0.57	0.51

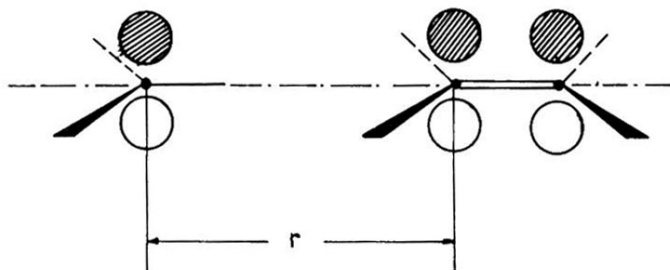


FIG. 5. OVA computations - transition state geometry and reaction coordinate (r).

The computed OV figures are collected in table 3.

According to procedure (4), one selects the OVA equation corresponding to $r = 3.2$.

Including electronic effects, via \mathcal{F}_C , one gets :

Table 3. OV(r) values

Alkene No.	OV(4.0)	OV(3.8)	OV(3.4)	OV(3.2)	OV(3.0)
1.	0.28	0.62	2.18	3.24	4.30
2.	0.28	0.62	2.18	3.24	4.30
3.	0.28	0.62	2.18	3.24	4.30
4.	0.28	0.62	2.18	3.24	4.30
5.	0.43	0.91	2.71	3.60	4.78
6.	0.43	0.91	2.71	3.60	4.78
7.	0.53	1.16	3.10	4.28	5.21
8.	0.53	1.16	3.10	4.28	5.21
9.	0.53	1.16	3.10	4.28	5.21
10.	4.12	4.92	7.00	8.17	9.26
11.	2.53	3.23	5.06	6.13	7.21

$$\log k_r = 0.856 - 0.288 \text{ OV}(3.2) - 0.782 \mathcal{F}_C \quad (13)$$

n	r	s	F	EV
11	0.82	0.48	4.90	0.60

The examination of the eq. (13) points out that the compounds 8 and 9 are not properly described by \mathcal{F} parameters. Rejecting these compounds the equation (13) becomes :

$$\log k_r = 1.047 - 0.286 \text{ OV}(3.2) - 1.320 \mathcal{F}_C \quad (14)$$

n	r	s	F	EV
9	0.94	0.30	13.0	0.85

The best E_S - type equation corresponding to the eq. (14) is :

$$\log k_r = -1.425 - 0.911 \mathcal{F}_C + 0.586 \sum E_S \quad (15)$$

n	r	s	F	EV
9	0.91	0.36	8.50	0.78

The two obtained equations compare well, the eq. (14) being slightly better. Both equations show that + I substituents increase the reaction rate, and the bulkier the substituent, the larger will be the decreasing of k_r .

6. Conclusions

i) OVA defines a principal new method to analyse quantitatively the steric effects in chemical reactions.

ii) OVA uses the minimum possible empirical information.

iii) OVA offers the possibility to take into account explicitly the reaction coordinate.

iv) It is no longer necessary to consider the substituent as having cylindrical symmetry (as implied by E_S - type methods).

v) Using OVA, one can consider in the computations the conformation of the substituent and the geometry of the transition state.

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