

CONFIGURATION OF $\text{VO}(\text{OR})_2\text{Cl}-\text{Al}(\text{i-Bu})_3$ CATALYST SYSTEM AND CHARGE DISTRIBUTION OF VANADIUM CENTRAL ION

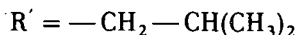
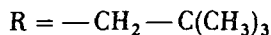
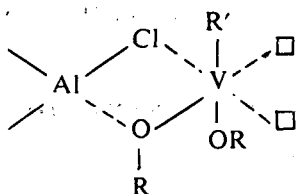
JIAO Shuke(焦书科), LU Chongxian(鲁崇贤) and JIANG Jian(姜 健)*

(Beijing Institute of Chemical Technology, Beijing)

ABSTRACT

According to the calculation of quantum chemistry it could be deduced that configurations of the catalysts $\text{VO}(\text{OR})_2\text{Cl}-\text{Al}(\text{i-Bu})_3$, for the alternating copolymerization of butadiene with propene, the highest reactive configuration was A. When the catalyst complex forms the configuration A, the energy of the system was the lowest; the central vanadium atom had relatively high positive charge and whose frontier orbital overlapped easily with the frontier orbital of butadiene to form coordination complex, so it was concluded from the experimental results and calculations that the configuration of the catalyst of relatively high activity was A.

In the previous paper^[1] dealing with the mechanism of alternating copolymerization of butadiene-propene based on $\text{VO}(\text{OR})_2\text{Cl}-\text{Al}(\text{i-Bu})_3$, the authors have reported that the active center of the catalyst is a regular octahedron complex with V^{+3} as central ion which has six ligands and the configuration of the complex was as follows:



The mechanism of alternating copolymerization caused by the catalyst system was also proposed. The purpose of this paper is to study and prove the configuration of the catalyst active center and the charge distribution of vanadium central ion based on quantum chemistry calculation and using Symmetry Conservation principle of molecular orbitals.

CALCULATION

By using QCPE-358 EHMO program the calculation was done on a Acos-4 computer (Japan)

Parameter Selection

- (1) EHMO parameter selection was listed in Table 1
- (2) Parameter selection of geometric structure: According to the reference^[2] the structural parameter selection of V^{+3} complex was listed in Table 2.
- (3) Standard data were used for other bond lengths and bond angles^[3].

Table 1 EHMO parameter

Orbit	$H_i(\text{eV})$	ρ_i
C 2s	-21.4	1.625
C 2p	-11.4	1.625
O 2s	-32.3	2.275
O 2p	-14.8	2.275
Cl 3s	-30.0	2.033
Cl 3p	-15.0	2.033
Al 3s	-12.3	1.167
Al 3p	-6.50	1.167
V 4s	-8.06	1.24
V 4p	-5.12	1.24
V 3d	-9.22	2.99

Table 2 The structural parameter of V^{+3} complex

Chemical bond	Bond length($\text{\AA}$)	Type of bond angle	Bond angle (degree)
V-Cl	2.398	< OVCl	98.5
V-O	1.862	< VClAl	81.5
V-C	2.217	< CAIC	128.5
Al-Cl	2.05(2.08)	< ClAlC	116.2
Al-O	1.864	< VOC	116.2
Al-C	1.965		
O-C	1.43		

CALCULATING RESULT

In order to simplify the calculation, when the calculation was done only the main atoms such as V, C, O, Cl were considered but not hydrogen atom (if hydrogen atom was included the energy of the system would change accordingly, but the changing sequence of their relative energies was not affected obviously.). According to the configuration of catalyst active center suggested in the reference^[1], the complex of V^{+3} was octahedron. V, Cl, O, Al and two vacant orbits of vanadium atom stayed in the same plane, neopentoxo, isobutyl connected with vanadium directly and situated above and below the plane where vanadium stayed. First, the space arrangement of neopentoxo and isobutyl was changed. Six different arrangements were selected (Figure 1). The calculating result was tabulated in Table 3.

For the convenience of description, A, B, C, D, E, and F were used to represent the six different configurations of the catalyst active center.

It could be seen from above data that when the configuration of the selected catalyst was A, D, E, or F the total energy of the system was always relatively low, and the positive charge of central vanadium atom was relatively high, both favored the process of catalyzing reaction. Therefore, we

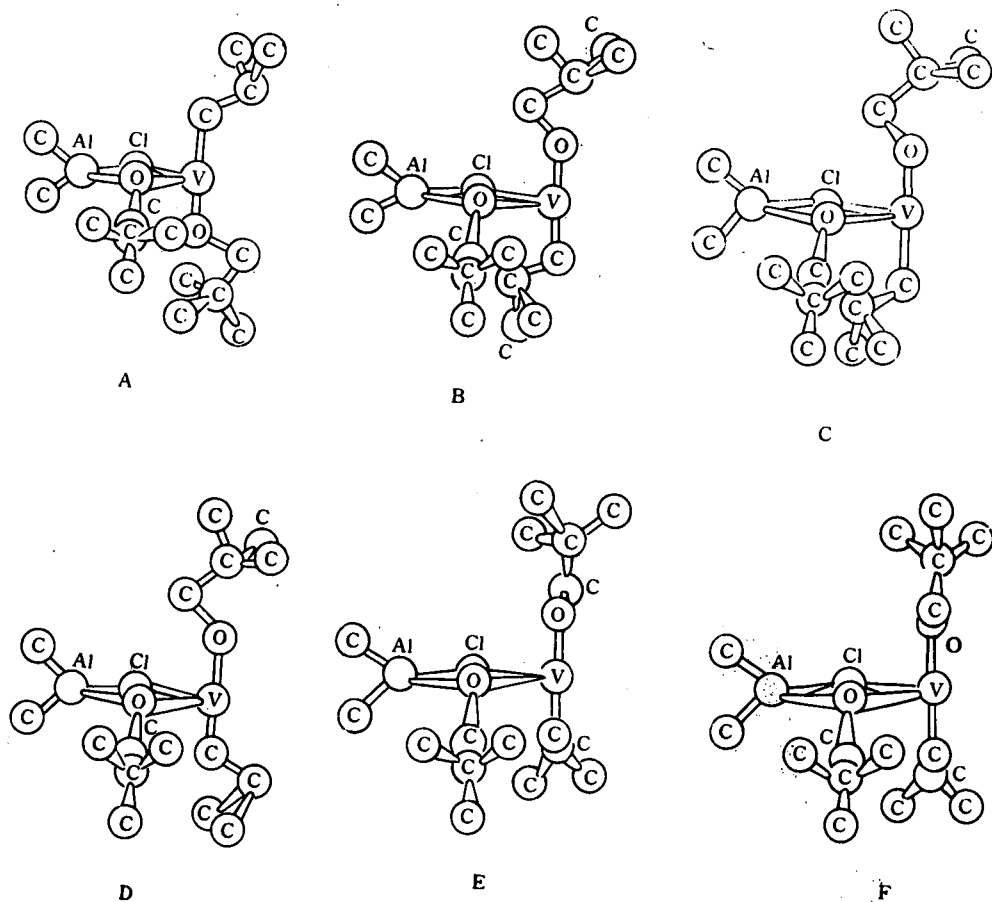


Figure 1 Six different space arrangements of V active center

selected any configuration from A, D, E and F, for instance, A was selected as the model of active center and $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{O}-$ was replaced by $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{O}-$ (A-1), $(\text{CH}_3)_2\text{CH}-\text{O}-$ (A-2), $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-\text{O}-$ (A-3), the obtained quantum chemistry calculating result was showed in Table 4.

It could be seen from the data in Table 4 that when $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{O}-$ of the configuration A of active center was replaced by $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{O}-$, $(\text{CH}_3)_2\text{CH}-\text{O}-$ or $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-\text{O}-$ the energy of the system was higher than that of A and the central vanadium atom became more negative. These factors were unfavorable to the catalyzing reaction.

When A was used as the model of the active center of the catalyzing reaction the butadiene molecule combined with two vacant orbits of the active center to form coordinating complex then isobutyl moved as an anion onto butadiene molecule and a vacant orbit left. Propene entered the vacant orbit and meanwhile the butadiene unit migrated from the central vanadium atom to the end of isopropyl group. There were two vacant orbits reformed on vanadium atom. The above process was repeated and resulted in propene-butadiene alternating copolymer. In order to describe this microcosmic process some calculation was done on coordinating complex formed from active center and butadiene, the intermediate (represented by A-A) formed after isobutyl anion migrated from central vanadium atom. isobutyl anion and propene molecule. The

Table 3 Calculating results of six stereomers

No. of The con- figuration	Total energy of active center (eV)	Electrical charge of V atom	The composition of Molecular Orbital of active center
A	-1946.11816	2.6034	$\psi_H = 0.9811\psi_{d_{xy}} + 0.1064\psi_{d_{x^2-y^2}}$ $\psi_I = 0.65194\psi_{d_{xz}} - 0.7573\psi_{d_{yz}}$
B	-1939.04785	0.7039	$\psi_H = 0.2051\psi_{d_{xz}} - 0.9673\psi_{d_{yz}}$ $\psi_I = 0.9687\psi_{d_{xz}} + 0.2053\psi_{d_{yz}}$
C	-1938.69971	0.7112	$\psi_H = 0.0869\psi_{d_{xz}} + 0.9900\psi_{d_{yz}}$ $\psi_I = 0.1341\psi_{p(0)x} + 0.986\psi_{d_{xy}} - 0.0848\psi_{d_{yz}}$
D	-1944.97314	2.6377	$\psi_H = 0.9848\psi_{d_{xy}} + 0.1094\psi_{d_{x^2-y^2}}$ $\psi_I = 0.6905\psi_{d_{xz}} - 0.7132\psi_{d_{yz}}$
E	-1945.64502	2.6529	$\psi_H = 0.9870\psi_{d_{xy}} + 0.1053\psi_{d_{x^2-y^2}}$ $\psi_I = 0.6597\psi_{d_{xz}} - 0.7446\psi_{d_{yz}}$
F	-1945.63770	2.6422	$\psi_H = 0.9857\psi_{d_{xy}} + 0.1063\psi_{d_{x^2-y^2}}$ $\psi_I = 0.7954\psi_{d_{xz}} + 0.5932\psi_{d_{yz}}$

Table 4 Quantum chemistry calculating result of the active center of A configuration

No. of The con- figuration	Total energy of active center (eV)	Electrical charge of V atom	The composition of Molecular Orbital of active center
A-1	-1766.79541	-1.3252	$\psi_H = 0.7497\psi_{d_{xz}} + 0.6443\psi_{d_{yz}}$ $\psi_I = 0.1268\psi_{p(0)x} - 0.1113\psi_{d_{xy}} + 0.9747\psi_{d_{x^2-y^2}}$
A-2	-1590.46240	-1.3297	$\psi_H = 0.7424\psi_{d_{xz}} + 0.6529\psi_{d_{yz}}$ $\psi_I = 0.1198\psi_{d_{xy}} - 0.9787\psi_{d_{x^2-y^2}}$
A-3	-1944.58545	-1.3410	$\psi_H = 0.7578\psi_{d_{xz}} + 0.6340\psi_{d_{yz}}$ $\psi_I = 0.1249\psi_{p(C)x} - 0.1076\psi_{d_{xy}} + 0.9984\psi_{d_{x^2-y^2}}$

calculating result was tabulated in Table 5 to Table 7.

Table 5 Quantum chemistry calculating result of A-A intermediate

Total energy of intermediate (eV)	Electrical charge of vanadium atom	Composition of Molecular Orbital of intermediate
-1945.95312	2.3923	$\psi_H = 0.5396\psi_{d_{xy}} + 0.7779\psi_{d_{yz}} + 0.3060\psi_{d_{xy}}$ $\psi_I = 0.3074\psi_{d_{xy}} + 0.1509\psi_{d_{yz}} - 0.9055\psi_{d_{xy}}$

Table 6 Quantum chemistry calculating result of isobutyl anion

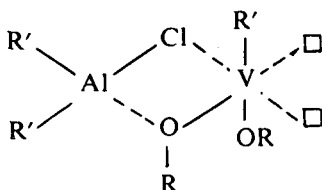
Total energy of isobutyl anion (eV)	Composition of Molecular Orbital of isobutyl anion
-423.26245	$\psi_H = 0.3282\psi_{p_x} + 0.4914\psi_{p_x} - 0.7718\psi_{p_y} - 0.2242\psi_{p_y}$ $\psi_I = 0.9948\psi_{s(H)} - 0.3966\psi_{s(C)} + 0.1385\psi_{p_y} + 0.6401\psi_{p_y} - 0.3002\psi_{p_z}$

Table 7 Quantum chemistry calculating result of propene molecule

Total energy (eV)	Charge distribution of carbon atom	Composition of molecular orbital
-303.32153	$C_1 = -1.0621$ $C_2 = -0.4513$ $C_3 = -0.2015$	$\psi_H = 0.4784\psi_{p_x} - 0.6631\psi_{p_x} + 0.4527\psi_{p_y}$ $\psi_I = 0.7854\psi_{p_z} - 0.8689\psi_{p_z}$

RESULTS AND DISCUSSION

(1) For the structure of the complex whose central atom was transition metal, regular octahedron and trigonal bipyramid were proposed, but there were only some experimental evidence for the former one. Basing on the reaction product of two component of the catalyst, spectral data and the theory of coordinating field, the following regular octahedron was deduced as the active center:



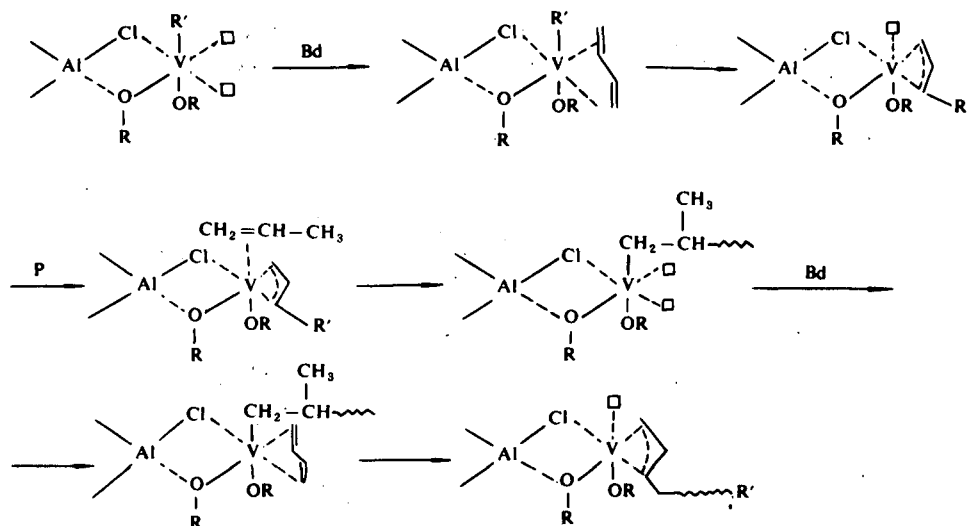
When R was $-\text{CH}_2-\text{C}(\text{CH}_3)_3$, R' was $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ the catalyst was active, while R and R' were replaced by other groups the activities dropped tremendously, even to zero. The experimental results^[1] were shown as follows:

R group	Conversion (% , 4hrs)
$(\text{CH}_3)_3\text{CCH}_2-$	80
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$	9.8
$(\text{CH}_3)_2\text{CH}-$	1.2

It could be seen from the above results that when R was $(\text{CH}_3)_3\text{C}-\text{CH}_2-$ and R' was $(\text{CH}_3)_2\text{CHCH}_2-$ and the selected configurations were A, D, E and F, the energies of the systems were low and stable, and the positive charge of the central vanadium atom was relatively high (see Table 3). This favored the attacking by butadiene molecule to make the reaction proceed easily. When R equaled to $(\text{CH}_3)_2\text{CHCH}_2-$, $(\text{CH}_3)_2\text{CH}-$, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$, the energies of the systems increased and the central vanadium atom had negative charge (see Table 4). Obviously, when the charge density of the central vanadium atom was relatively high it was difficult for the butadiene molecule to attack the vanadium atom to make the reaction go on. It was concluded that the theoretical calculation could be compared with the experimental results.

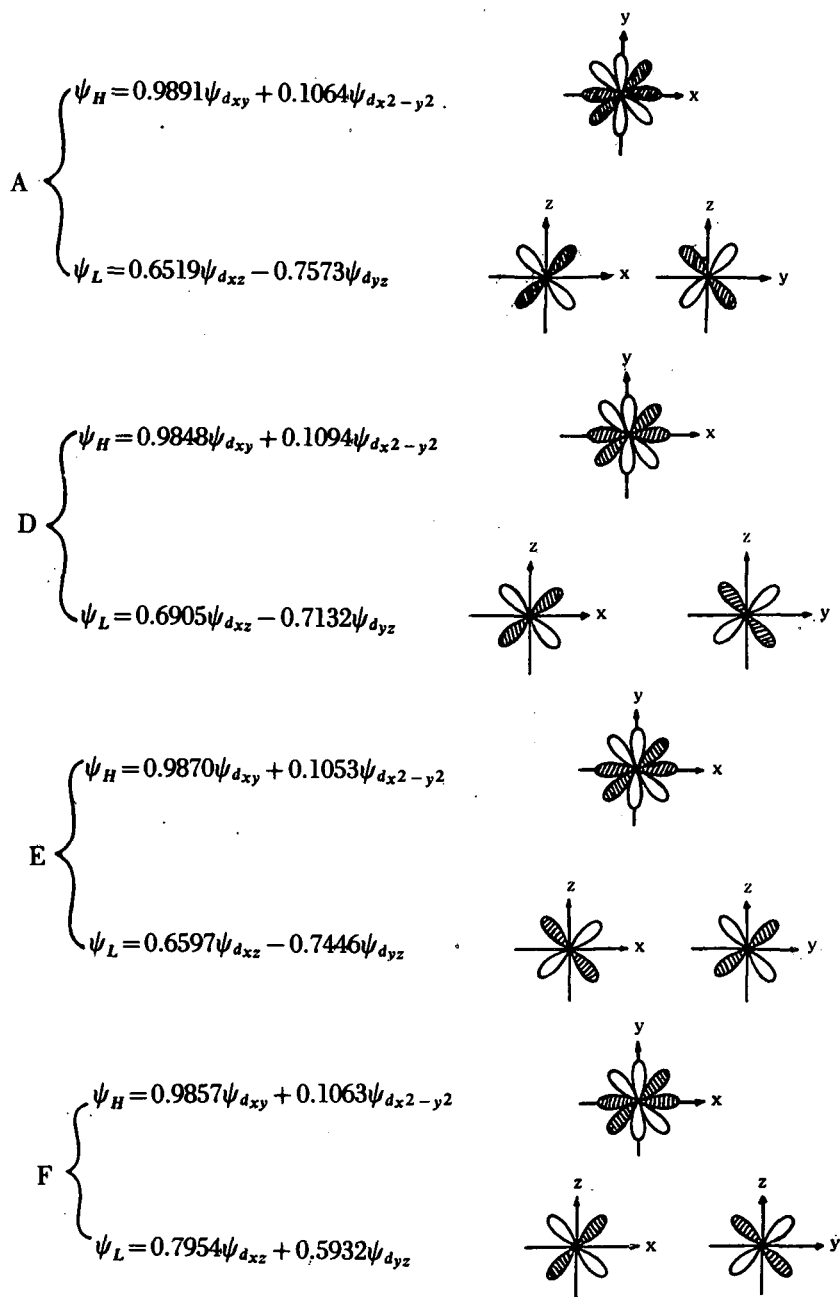
(2) Butadiene combined with the active center of the catalyst to form a complex, in which the isobutyl anion migrating onto the butadiene end and left a vacant orbit to form a new active center represented by A-A. It was proved by the quantum chemistry calculation on A-A that: the energy of A-A system was relatively low and stable so it was easy to form A-A system. There was relatively high positive charge on central vanadium atom which also favored the attack by propene molecule to make the reaction be continued easily.

(3) In the previous paper[1], the authors proposed the mechanism of the reaction as follows:



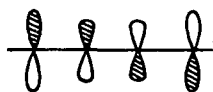
From this reaction mechanism it could be seen that when chain initiation occurred, the molecular orbital of butadiene functioned with the molecular orbital of the catalyst and R' migrated to leave vanadium atom a vacant orbit which then functioned with the orbit of propene molecule. The process was repeated to obtain the alternating copolymer of butadiene and propene. The calculation of quantum chemistry and symmetric conservation principle of molecular orbital were used to probe the microcosmic process.

By calculating on active center with A, D, E and F configuration which had catalyzing activities, the frontier orbitals and the figures were obtained as follows:

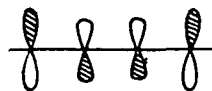


Molecular orbital of butadiene molecule:

$$\psi_H = 0.6015\phi_1 + 0.3717\phi_2 - 0.3717\phi_3 - 0.6015\phi_4$$

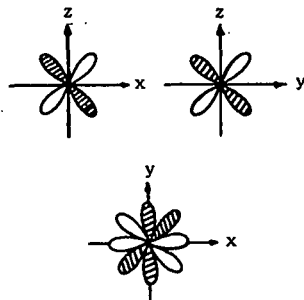


$$\psi_I = 0.6015\phi_1 - 0.3717\phi_2 - 0.3717\phi_3 + 0.6015\phi_4$$

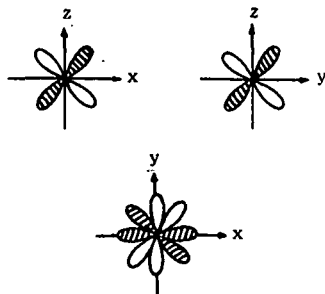


When the configuration of catalyst was fixed as A and R group changed from $(\text{CH}_3)_3\text{C}-\text{CH}_2-$ to $(\text{CH}_3)_2\text{CHCH}_2-$, $(\text{CH}_3)\text{CH}-$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ respectively, A-1, A-2 and A-3 configurations were obtained accordingly. By calculating on these configurations the frontier orbitals and figures were as follows:

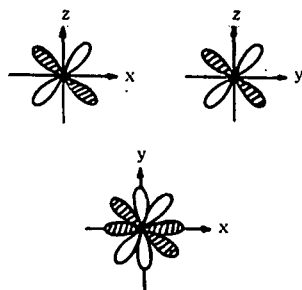
$$\text{A-1} \begin{cases} \psi_H = 0.7497\psi_{d_{xz}} + 0.6443\psi_{d_{yz}} \\ \psi_L = 0.1268\psi_{p(0)x} - 0.1113\psi_{d_{xy}} + 0.9747\psi_{d_{x^2-y^2}} \end{cases}$$



$$\text{A-2} \begin{cases} \psi_H = 0.7424\psi_{d_{xz}} + 0.6529\psi_{d_{yz}} \\ \psi_L = 0.1198\psi_{d_{xy}} - 0.9787\psi_{d_{x^2-y^2}} \end{cases}$$



$$\text{A-3} \begin{cases} \psi_H = 0.7578\psi_{d_{xz}} + 0.6340\psi_{d_{yz}} \\ \psi_L = 0.1249\psi_{p(C)x} - 0.1076\psi_{d_{xy}} + 0.9784\psi_{d_{x^2-y^2}} \end{cases}$$



According to the symmetric conservation principle of molecular orbital, when two molecules reacted, the molecular orbital of the highest occupied molecular orbital of one of the molecule (HOMO) had to have the same phase or reverse phase with the molecular orbital of the lowest unoccupied molecular orbital of the other molecule. Only when (+) lobe of these orbits overlapped with (+) lobe and (-) lobe with (-) lobe did the reaction occur.

It could be seen from the calculating result that for the active centers of A, D, E and F configurations, their frontier orbital composed mainly of d orbits of vanadium atom and the orbits of other atoms contributed very little. If these frontier orbitals, such as the molecular orbitals of the highest occupied, matched with the lowest unoccupied molecular orbital of butadiene in symmetry, it was easy for the orbits to overlap to make the reaction go on. While the frontier

orbitals of the active center of A-1, A-2 and A-3 configurations such as the molecular orbital of the highest occupied electron, did not match with the lowest unoccupied molecular orbital of butadiene in symmetry so it was difficult for the orbits to overlap and for the reaction to occur.

By calculating on the active center A-A, propene molecule and isobutyl anion, the frontier orbitals and figures were obtained as follows:

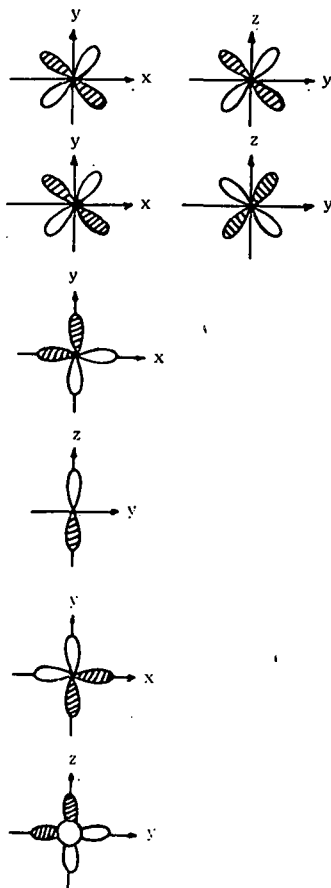
$$\text{A-A} \begin{cases} \psi_H = 0.5396\psi_{d_{xz}} + 0.7779\psi_{d_{yz}} \\ \psi_L = 0.3074\psi_{d_{xz}} - 0.9055\psi_{d_{xy}} \end{cases}$$

Propene molecule:

$$\begin{cases} \psi_H = 0.1847\psi_{p_x} - 0.4527\psi_{p_y} \\ \psi_L = 0.0243\psi_{p_z} \end{cases}$$

Isobutyl anion:

$$\begin{cases} \psi_H = 0.8193\psi_{p_x} - 0.9960\psi_{p_y} \\ \psi_L = 0.9948\psi_{s(H)} - 0.3966\psi_{s(C)} + 0.7786\psi_{p_y} - 0.3002\psi_{p_z} \end{cases}$$



It was easy for the frontier orbital of active center to overlap with the frontier orbital of propene molecule to form coordination complex so the reaction could be continued to produce the desired product.

CONCLUSION

According to the calculation of quantum chemistry it could be deduced that in the alternating copolymerization reaction of butadiene and propene, among the configurations of the catalysts $\text{VO}(\text{OR})_2\text{Cl}-\text{Al}(\text{i-Bu})_3$, the configuration with the highest activity was A. When the configuration of the catalyst was A the energy of the system was the lowest; the central vanadium atom had relatively high positive charge and whose frontier orbital overlapped easily with the frontier orbital of butadiene to form coordination complex, so it was concluded from the experimental result that the configuration of the catalyst of relatively high activity was A.

Keywords:

Energy of catalyst complex; Charge distribution of catalyst center ion; Configuration of vanadium catalyst; Quantum chemistry calculation of catalyst system

REFERENCES

- [1] JIAO Shuke, YU Dingsheng and QI Yincheng, *Chemical Journal of Chinese Universities*, **1982** 3(1), 67.
- [2] Haaland, A. and Stokkeland, O., *Journal of Organometallic Chemistry*, **1975**, 94, 348.
- [3] Pople, J.A. and Beveridge, L., "Approximate Molecular Orbital Theory", McGraw-Hill Book Co., New York **1970**.