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ISOMERIC ACTIVE ENDS OF GROWING CHAINS IN THE CATIONIC POLYMERIZATION OF 4-METHYL-1-PENTENE

QUANTUM CHEMICAL INVESTIGATION

V. YA. BOGOMOLNYI, YU. YE. EIZNER and S. S. SKOROKHODOV
Institute of High Molecular Weight Compounds, Academy of Sciences of U.S.S.R., Bolshoi pr. 31, Leningrad 199004, U.S.S.R.

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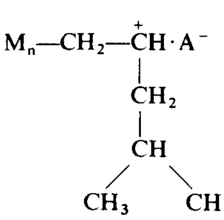
Abstract—Quantum chemical investigation of the relative stabilities of carbenium ions modelling the end units of growing chains in the cationic polymerization of 4-methyl-1-pentene has been carried out. The investigation was performed by the CNDO/2 method and by partial optimization of geometry. It is shown that the polymer chain can be adequately modelled by a methyl group. The calculated values of relative energies ΔE, geometric parameters and charge distribution are given for free cations, ion-pairs and for the cation-electron donor and cation-electron acceptor systems (H_2O, HCN and NO_2). All the additives show donor behaviour with respect to cations. The differences in the energies of secondary and tertiary cations decrease on going from free ions to ion-pairs or cation-additive molecule system.

The cationic polymerization of α-olefins still attracts attention [1]. The problem of synthesis of high molecular weight poly-α-olefins is now partly solved, e.g. for 4-methyl-1-pentene (4M1P) as shown by Kennedy [2], Cesca [3] and some of the present authors [4]. The new details of the structure of cationic poly 4M1P and influence of the solvent polarity and temperature of polymerization have recently been shown by Cesca [3]. However, the problem of regulation of the isomeric structure of the polymer chain is still very complicated. For simplicity, we consider only three types of structure for poly 4M1P.

The normal addition of monomer to the active end of the chain corresponds to secondary cation I (M_n is a model for the polymer chain, A^- is that for the counter-ion). Before the addition of the next monomer, the macrocation of type I can rearrange to a more stable cation (type II) or to some more stable tertiary cation (type III).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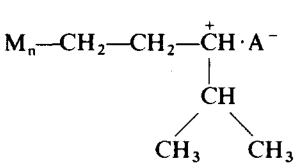
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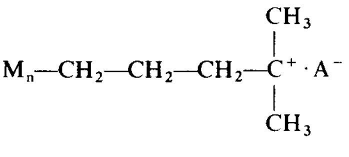
III

The most important factor influencing the isomerization polymerization seems to be the kinetic control. This effect is observed when the content of monomer units of type 1,4 increases owing to a decrease in the initial monomer concentration [4]. Another factor is the solvation of the active centre by ligands of various nature (solvents or additives). The influence of solvation on the structure of the polymer chain can be analysed on the basis of published experimental data [4, 5]. Nevertheless, this attempt does not permit any definite conclusions.

The difficulties in the determination of the structure of the polymers and in the interpretation of the experimental data suggested a detailed quantum chemical investigation of the electronic structure and energy of various types of active centres in the cationic polymerization of α-olefins in particular 4M1P.

We investigated the relative stabilities of all three isomeric types of the end unit of the growing polymer chain. We also studied the influence of two factors on the stability of isomeric cations:

(1) dissociation (free ions and ion-pairs with counter-ion $A^{\ominus}$) and

(2) formation of a complex of the active centre and the added molecule of a basic or acidic ligand.

The quantum chemical investigation of the polymerization reactions and the possibilities and limitations of this approach have been considered [6].

The calculations were carried out by the CNDO/2 method, using standard parametrization [7, 8] and only *s*- and *p*-atomic orbitals of the valence shell of atoms. The search for the minimum of the total energy of the molecule as a function of some bond lengths, valence angles and rotation angles was carried out by the Powell conjugated gradient method [9]. Other geometric parameters were not optimized and "standard" values were used [10] (see also [11]).

We deliberately used for calculation the simplest molecules presenting two types of active chain ends, viz. free cations and ion-pairs (with counter-ion Cl^-). The quantum chemical approach and the choice of subjects led to a grossly exaggerated difference in stability between the cations as compared to the real systems, where strong solvation effects exist. An alkylchloride is a very approximate model for the ion-pair because of the low polarity of the C—Cl bond which prevents polymerization in common solvents. The choice of model ligands (H_2O, HCN, NO_2) was made for simplicity.

FREE CATIONS

The optimized geometric parameters of cations I, II, and III include: bond length $r(C_t - C_M)$, $r(C_t - C_R)$ and $r(C_t - H)$ between the terminal positively charged carbon atom C_t on the one hand and the neighbouring carbon atom in the main chain C_M and the side group C_R and hydrogen atom on the other hand and also angle ϑ between any of these bonds and the extension of the axis of the pyramid formed by them and supposed equiangular.

As might be expected, angle ϑ is 90°. The values of the bond length *r* in Å and atomic charges q on the atoms considered are given in Table 1. The relative energies of isomeric cation ΔE in kcal/mol relative to the less stable cation (with the same M_n) are shown in Table 1.

These calculations show the influence on the final results of the length of the substituent M_n modelling the polymeric chain. This relation is important as such, but it is of special interest for our investigation. Indeed, the influence of the length of M_n in different isomeric cations must vary because of the different distances between C_t and M_n i.e. two, three and four bonds in cations I, II and III, respectively. The data in Table 1 show this variation and make it possible to make some recommendations. If the values of errors δ_r, δ_q and $\delta_{\Delta E}$ (approximately 0.01 Å, 0.01 a.u. of charge and 2 kcal/mol respectively) are accepted, then methyl group can be used as a chain model. For searching for the stable geometry it is possible to use even $M_n = H$. We suppose that more precise determinations are not necessary because of the approximate nature of the CNDO/2 method for estimation of the values of r and ΔE (see [6]). The second reason for approximated calculations is that the variations of the value of charges produced by the internal rotation of an alkyl group in molecules are of the same order of magnitude as the errors [12]. Nevertheless, these errors are so low that it is possible to distinguish correctly the electronic structures and energies of various isomeric cations under consideration. The sequence of values of ΔE shown in Table 1 demonstrates the well known dependence of the stability of the cations on the degree of substitution of the charged carbon atom and the branching of substituent groups. It shows that the CNDO/2 method is suitable for calculation of these cations. It should be noted that the higher is the stability of the end cationic group, the greater is the part of the charge of the macrocation concentrated on it.

SYSTEMS CATION-COUNTER-ION, CATION-LIGAND AND CATION-COUNTER-ION-LIGAND

The geometry of ion-pairs of the type $Cat^{\oplus}\ Cl^{\ominus}$, where $Cat^{\oplus}$ was one of the cations $[CH_3 - C_6H_{13}]^{\oplus}$ was optimized additionally by searching for the location of the Cl-atom. It was shown that $Cl^{\ominus}$ was always

Table 1. Geometry and electronic structure of cations

Isomer	M_n	ΔE	Bond length* $C_t - C_M$	Bond length* $C_t - C_R$	Bond length* $C_t - H$	Atomic charges C_t	Atomic charges C_M	Atomic charges C_R	Atomic charges H	†
I	H	0	1.430	1.440	1.082	+0.342	−0.099	−0.057	+0.079	+0.857
	CH_3	0	1.427	1.442	1.082	+0.328	−0.033	−0.055	+0.075	+0.839
	C_2H_5	0	1.427	1.442	1.082	+0.321	−0.037	−0.053	+0.073	+0.810
	i-C_3H_7	0				+0.317	−0.036	−0.052	+0.073	+0.792
II	H	−14.6	1.444	1.425	1.082	+0.321	−0.053	+0.012	+0.073	+0.952
	CH_3	−8.0	1.444	1.425	1.082	+0.318	−0.060	+0.011	+0.072	+0.941
	C_2H_5	−6.0				+0.318	−0.063	+0.011	+0.071	+0.926
	i-C_3H_7	−5.1				+0.316	−0.064	+0.011	+0.071	+0.919
III	H	−43.3	1.456	1.448		+0.332	−0.060	−0.091 −0.088		+0.966
	CH_3	−34.2	1.456	1.448		+0.332	−0.064	−0.091 −0.088		+0.963
	C_2H_5	−31.8				+0.332	−0.064	−0.091 −0.088		+0.950
	i-C_3H_7	−30.1				+0.332	−0.063	−0.091 −0.088		+0.946

* The values of bond length are not given, if increase of M_n is not followed by additional optimization of the geometry. † Total charge of end monomer unit C_6H_{12}.

Table 2. Geometry, charge distribution and relative energies of model free cations interacting with counter-ion and additives

A	L	Isomer	ΔE	ϑ	$r(C_t - C_m)$	$r(C_t - C_R)$	$r(C_t - H)$	$r(C_t - Cl)$	r_L	q_{C_t}	q_{Cl}	q_L	P_{C_t-Cl}	P_L
		I	0	90	1.43	1.44	1.08			+0.33				
		II	−8	90	1.44	1.42	1.08			+0.32				
		III	−34	90	1.46	1.45				+0.33				
Cl		I	0	108	1.48	1.49	1.09	1.61		+0.09	−0.07		0.96	
		II	−3	108	1.49	1.49	1.09	1.61		+0.09	−0.07		0.96	
		III	−6	106	1.49	1.48		1.62		+0.10	−0.08		0.92	
	H_2O	I	0	105	1.48	1.49	1.09		1.45	+0.22		+0.48		0.70
		II	−4	105	1.48	1.49	1.09		1.45	+0.21		+0.48		0.70
		III	−12	104	1.49	1.48			1.46	+0.24		+0.44		0.64
	HCN	I	0	107	1.48	1.49	1.09		1.40	+0.12		+0.56		0.89
		II	−2	107	1.49	1.49	1.09		1.40	+0.12		+0.56		0.89
		III	−8	105	1.50	1.48			1.41	+0.16		+0.53		0.85
Cl	H_2O	I	0						1.87	+0.06	−0.02	+0.01	0.94	0.04
		II	−3						1.86	+0.06	−0.01	+0.01	0.94	0.04
		III	−7						1.78	+0.06	−0.01	+0.02	0.89	0.06
Cl	O_2	I	0						1.70	+0.07	+0.04	−0.14	0.78	0.25
		II	−3						1.70	+0.06	+0.04	−0.14	0.78	0.25
		III	−9						1.69	+0.10	+0.04	−0.14	0.71	0.29

r_L-The distance from nearest to C_t atom of ligand to Cl, for free cation-C_t − L, q-atomic charge (q_L-total charge of molecule of ligand); P_{xy}-the Wiberg order of the bond x–y [13] (P_L—the order of the bond L—Cl, L—C_t) L-atom of ligand nearest to C_t.

situated on the axis of the pyramid formed by bonds adjacent directly to $C_t^{\oplus}$. The angle between this axis and the direction of bond $C_t^{\oplus}$—$Cl^{\ominus}$ did not exceed 5°. In systems of the type $Cat^{\oplus}L$, the molecule of ligand L was always situated on this axis in such a manner that their symmetry axis coincided with that of the pyramidal cation structure. Heteroatoms O, N and N in H_2O, HCN and NO_2, respectively, were directed to C_t and the distance $C_t \ldots O(N)$ was optimized. In systems of the type $Cat^{\oplus}Cl^{\ominus}L$, the geometry was not additionally optimized for $Cat^{\oplus}Cl^{\ominus}$. The additional optimization was performed by the search of the location and direction of L. It was estimated that the location and orientation of L virtually coincide with the arrangement calculated for $Cat^{\oplus}L$. The results of this calculation are given in Table 2 (including the data for $M_n = CH_3$ from Table 1).

The data obtained show first that the interaction of cations with the counter-ion and with neutral ligands of donor or electron acceptor nature has the same influence on the cations. In these three cases the isomeric relations, the geometry and the charge distribution of the end unit change identically. This means that not only the anion but also any neutral molecule behaves as an electron donor with respect to the cation. The macrocation takes from 0.4 to 0.9 of the electron charge; the geometry of its terminal carbon atom $C_t^{\oplus}$ changes from coplanar typical of cations ($\vartheta = 90°$) to almost tetrahedral ($\vartheta = 109.47°$). All three bonds adjacent to C_t become longer, probably owing to a change in the hydridization of C_t from sp^2 to sp^3. As a result, the differences in the stability of the isomeric cations become less pronounced. It should be noted that the increase in stability by branching is typical of cations but not of neutral molecules. As the interaction of a free cation with an anion or a ligand leads to the transformation of sp^2-geometry to sp^3, the action of the next molecule has virtually no influence on the cationic system (see Table 2, lines 5 and 6). This sharp difference in the behaviour of free cations and ion-pairs and cation + ligand systems permits the following assumption. Free cationic polymerization of 4MIP should lead to a more pronounced tendency to increasing content of the 1,3- and 1,4-units in the polymer chain. This assumption is true if the system is not kinetically controlled. The kinetic factor must have the reverse effect. The problem needs further investigation. It should be noted that published data [3, 4] show a higher content of the rearranged units in poly 4M1P obtained in polar solvents than in nonpolar solvents. It is also of interest that we could not change the structure of poly 4M1P by the addition of electron donors and electron acceptors to the initial polymerizing mixture [14]. A more adequate comparison of theoretical and experimental data would be possible by investigating the free-cationic polymerization of α-olefins, for instance, under the influence of γ-radiation or photoionization [1] or by nuclear chemical initiation [15].

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