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Electronic Transitions in Catalyst Systems

Olefin Polymerization by Titanium Trichloride-Aluminum Alkyl*

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The electronic energy levels were calculated for the molecular orbitals of the octahedral complex, $RTiCl_4$-olefin, which is postulated to be an intermediate in polymerization by $TiCl_3$-aluminum alkyl catalyst systems. In this complex, an electronic transition from the highest filled orbital to the half-filled orbital above corresponds to the initial step in the olefin insertion reaction which has been proposed by many as the propagation step in the polymerization. The energy of this transition was calculated to be near the known values of 10-14 kcal/mole for the activation energy of the polymerization reaction. Consequently, this suggests that the electronic transition may be the controlling step in the reaction.

The calculated electronic energy levels for the octahedral complex, $CH_3CH_2TiCl_4$, and the tetrahedral complex, CH_3TiCl_3, were used to judge the relative stability of these complexes. In both complexes, the lowest electronic transition corresponds to an initial step in the breaking of the Ti–C bond. For CH_3TiCl_3, the energy of this transition is 3.2 eV, which is much too high for thermal excitation and probably accounts for its known stability. The energy of the corresponding transition in $CH_3CH_2TiCl_4$ is 1.07 eV, which indicates that this complex is much less stable than CH_3TiCl_3. However, the transition is high enough to account for the stability of the complex under polymerization conditions in the absence of olefins.

The electronic energy levels were calculated by use of an IBM computer program designed by Professor R. Hoffman, Cornell University, and based upon the linear combination of atomic orbital–molecular orbital method with a modified form of the Wolfsberg-Helmholz approximation.

I. INTRODUCTION

Often catalytic reactions can be described by a sequence of separate reaction steps. Although each of the intermediates in the sequence is unstable, a certain activation energy is required for the reaction to proceed from one intermediate to the next. Apparently little work has been done to determine whether any correlation exists between activation energy and electronic transition energy in the intermediate reaction complexes, and to correlate structure of catalyst complexes and catalyst selectivity. Semiempirical molecular orbital calculations, which have been applied with various degrees of success to the study of the electronic properties of simple compounds, appear particularly attractive for the elucidation of electronic structure of catalyst systems. As the semiempirical methods undergo improvements and refinements, such an approach should prove increasingly useful.

This paper describes the application of a simple semiempirical method to the olefin polymerization by organometallic catalyst systems. Several investigators have studied the mechanism of polymerization by or-

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ganometallic catalyst systems (*1–8*). It is generally agreed that the monomer molecule inserts between a metal atom and a carbon atom of an organometallic complex. Cossee (*9, 10*) has used the concepts developed in ligand-field theory and molecular orbital methods to describe the bonding and possible electronic transitions which lead to polymerization via the catalyst complex. In the present study, the Cossee polymerization model is studied by calculating the one-electron molecular orbital energies in the octahedral complexes, $RTiCl_4$ and $RTiCl_4$-olefin. Furthermore, the possible transitions in the tetrahedral complex, CH_3TiCl_3, are calculated and discussed in terms of stability for the complex. The experimentally observed electronic transitions in $TiCl_4$ were compared with the corresponding calculated values to check the possible reliability of the calculations.

The calculations were performed by use of an IBM computer program developed by Hoffman (*11*) and based upon a modified form of the Wolfsberg-Helmholz (*12*) approximations for the molecular orbital calculations.

II. Procedure

In each of the calculations the coordinate system was common to all atoms in the molecular complex. The arrangement and numbering of the atoms and the interatomic distances used are shown in Figs. 1 and 2, or are given in the discussion.

The atomic orbitals used in the construction of the one-electron molecular orbitals were 3*d*, 4*s*, and 4*p* of titanium, 3*s* and 3*p* of chlorine, and 2*s* and 2*p* of carbon. The titanium radial wave functions were those for the neutral atom published by Richardson *et al.* (*16, 17*). The double-ζ functions given by Clementi (*15*) were used for chlorine and carbon.

The diagonal elements, H_{ii}, for the titanium atom were approximated as valence state ionization energies (VSIE), which were obtained using the values and method given by Ballhausen and Gray (*13*). The diagonal elements for chlorine were taken to be 12.1 eV for the 3*p* orbitals and 23.7 eV for the 3*s* orbitals. The 3*p* diagonal element was estimated from the ionization energy of $TiCl_4$ (*21*). The 3*s* diagonal element was obtained by assuming that the difference in the Coulomb energies of the 3*p* and 3*s* levels was 11.6 eV, the same as the difference between the two $^3P_2$ states having the configurations $3s^23p^4$ and $3s3p^5$ (*18*). The Coulomb energies of the carbon 2*p* orbital were assumed to have the same absolute value as the ionization energies of the appropriate alkyl radical or olefin molecule (*19*). The 2*s* Coulomb energy was taken to be 21.0 eV.

The nondiagonal elements, H_{ij}, were

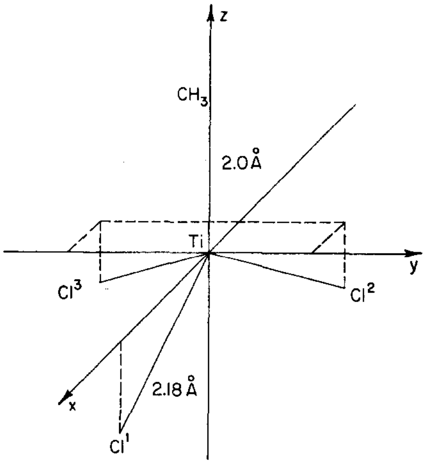

FIG. 1. Molecular configuration for CH_3TiCl_3.

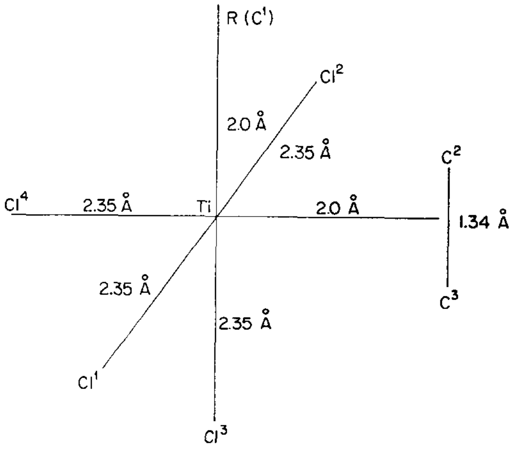

FIG. 2. Molecular configuration for the complex $RTiCl_4$ (olefin).

obtained by the method of Wolfsberg and Helmholz (*12*), using the approximation

$$H_{ij} = \tfrac{1}{2}[F(H_{ii} + H_{jj})S_{ij}] \qquad (1)$$

However, F was not kept constant, but it was made a function of the two Coulomb energies according to the relationship

$$F = 2(H_{ii}/H_{jj})^{1/2} \qquad (2)$$

where H_{ii} is the higher and H_{jj} the lower level of H_{ii} and H_{jj}. This modification was made to take into account the decrease of the resonance energy as the difference between H_{ii} and H_{jj} becomes greater. For $TiCl_4$, calculations were also made using the unmodified Wolfsberg-Helmholz approximation [Eq. (1)] and the approximation of Ballhausen and Gray in which the geometric mean replaces the arithmetic mean in Eq. (1). The results obtained by the three methods are compared in the following section.

The one-electron molecular orbital energies were calculated using a computer program supplied by Hoffman (*11*). The original program was limited to the use of Slater wave functions for every orbital except one for each atom of the system. For the one exception a linear combination of Slater-type functions could be used with a limit of five terms. For this study the program was modified to permit the use of expanded wave functions with as many as five terms for all orbitals. Additional modifications in the program were made to permit the calculation of a self-consistent charge on the central atom. In this procedure a charge on Ti was assumed initially, and after one cycle of calculation, a charge distribution was obtained by means of Mulliken's electron population analysis; the calculated charge was then used in the following cycle and the iteration was repeated until self-consistency was achieved. A difficulty with the Mulliken population analysis is the occurrence of negative elements in the charge matrix. Mulliken attributed this anomaly to imperfections in the definitions of the population distribution. Since a negative electron population is devoid of physical meaning, the program was modified so that all negative elements in the charge matrix were deleted, and the charge matrix was then normalized.

III. MOLECULAR ORBITAL ENERGIES OF $TiCl_4$

Electron diffraction measurements (*23*) show that $TiCl_4$ has a regular tetrahedral structure with bond distances, 2.18 Å. The electronic absorption spectrum of $TiCl_4$ between 14 and 47 kK has been reported (*20*). It shows two bands, 35.65 and 43.15 kK, which have been assigned (*20*) to the $t_1 \rightarrow 2e$ and the $t_1 \rightarrow 4t_2$ transition, respectively. However, no other bands are observed between 47 and 50 kK, and it seems possible that the $3t_2 \rightarrow 2e$ transition is also contained under the higher frequency band.

Using the experimentally determined geometry and bond length, several calculations of the electronic energy levels of $TiCl_4$ were made. These differed only in the method of estimating the off-diagonal elements in the energy matrix. The results of these calculations are shown in Table 1. The orbital energies given in the first column of the table were obtained by estimating H_{ij} according to Eq. (1), with $F = 2$; those given in the second column were obtained using the approximation (*13*) $H_{ij} = -F'(H_{ii}H_{jj})^{1/2}S_{ij}$, again with $F' = 2$; and those in the third column were obtained using Eq. (1) and (2).* The calculated excitation energies, taken simply as orbital energy differences, are compared with the spectroscopic values in Table 2.

With the exception of the order of the $1e$ and $2a_1$ orbitals, the three methods yield the same arrangement of molecular energy levels. However, the numerical values of the levels vary appreciably. The first two methods yield not only much higher energies of transition than observed, but also too large a value of Δ, the energy separation between the $2e$ and $4t_2$ orbitals. The spectroscopic value of Δ was taken as the difference between the wave numbers

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* Calculations were also made "using" the approximation to the off-diagonal matrix element introduced by L. C. Cusachs [*J. Chem. Phys.* **43**, 5157 (9565)], $H_{ij} = 1/2\ (H_{ii} + H_{jj})\ S_{ij}\ (2 - S_{ij})$. The results obtained were similar to those obtained using Eq. (1).

TABLE 1

ELECTRONIC ENERGY LEVELS (eV) FOR $TiCl_4$

H_{ij} by Wolfsberg-Helmholz approximation		Electronic configuration	H_{ij} by Gray-Ballhausen approximation		H_{ij} by modified Wolfsberg-Helmholz approximation		Electronic configuration
$3a_1$	+15.38		$3a_1$	+10.51	$3a_1$	− 0.84	
$5t_2$	− 1.72		$5t_2$	− 3.42	$5t_2$	− 5.09	
$4t_2$	− 3.24		$4t_2$	− 3.73	$4t_2$	− 6.08	
$2e$	− 5.78		$2e$	− 5.99	$2e$	− 6.93	
t_1	−11.64	XXXXXX	t_1	−11.64	t_1	11.64	XXXXXX
$3t_2$	−12.38	XXXXXX	$3t_2$	−12.41	$3t_2$	−12.42	XXXXXX
$2t_2$	−13.05	XXXXXX	$2t_2$	−13.09	$2t_2$	−12.94	XXXXXX
$2a_1$	−13.32	XX	$2a_1$	−13.45	$1e$	−13.52	XXXX
$1e$	−13.70	XXXX	$1e$	−13.80	$2a_1$	−13.64	XX
$1t_2$	−24.02	XXXXXX	$1t_2$	−23.80	$1t_2$	−23.85	XXXXXX
$1a_1$	−25.12	XX	$1a_1$	−24.51	$1a_1$	−24.44	XX
Charge on Ti	+0.37			+0.47		+0.6	
Coulomb energies 3d	−9.41			−9.70		−10.0	
4s	−8.58			−8.86		−9.19	
4p	−5.10			−5.47		−5.89	

of the two charge-transfer bands. The results could not be improved by variations in the empirical constants F and F'. For example, when the value of F' was decreased to 1.75, the energy of the $t_1 \rightarrow 2e$ transition became 4.3 eV, which compares favorably with the experimental value, but that of the $t_1 \rightarrow 4t_2$ transition was 7.2 eV, and Δ increased to 2.9 eV. The third method yields results in good agreement with the experimental data. This method was also used to calculate the molecular orbital energies of $TiBr_4$. The calculated results were 4.06 eV for the $t_1 \rightarrow 2e$ transition and 4.94 eV for the $t_1 \rightarrow 4t_2$ transition; the corresponding experimental values are (*20*) 3.44–3.64 eV, and 4.45 eV.

The calculations of the one-electron molecular orbital energies of $TiCl_4$ and $TiBr_4$ were made mainly to test, by comparison with the spectroscopic data, the reliability of the calculation method and the adequacy of the basis set and radial wave functions used. In view of the results obtained, the Wolfsberg-Helmholtz method modified according to Eq. (2) was used in subsequent calculations.

IV. ELECTRONIC STRUCTURE FOR CH_3TiCl_3 —RELATIONSHIP WITH STABILITY

The Cossee polymerization model is based upon the premise that the Ti–C bond in the catalyst complex is weak and can be broken during the olefin insertion process. In this regard, it is of interest to examine the electronic structure for CH_3TiCl_3 to

TABLE 2

CALCULATED AND EXPERIMENTAL EXCITATION ENERGIES (eV) IN $TiCl_4$

Transition	Observed	Calculated		
		W-H	B-G	Modified W-H
$t_1[{}^1A_1] \rightarrow 2e[{}^1T_2]$	4.42	6.01	5.73	4.74
$t_1[{}^1A_1] \rightarrow 4t_2[{}^1T_2]$	5.35	8.36	7.81	5.56
$\Delta(2e \rightarrow 4t_2)$	0.93	2.35	2.08	0.85
$3t_2[{}^1A_1] \rightarrow 2e[{}^1T_2]$	5.35	6.6	6.42	5.49

determine whether or not the relative strength of the Ti–C bond in this compound could be predicted. Beermann and Bestian (*22*) have prepared and isolated CH_3TiCl_3. It has a melting point of 28–29°C and a boiling point of 120°C (extrapolated vapor pressure curve). Below its decomposition temperature, pure methyltitanium trichloride in hydrocarbon solutions is not a catalyst for ethylene polymerization (*22*, *27*). However, it becomes an active catalyst when heated above its decomposition temperature, or upon addition of aluminum alkyls, VCl_4, or $VOCl_3$ (*27*). Its catalytic activity is not affected by addition of $TiCl_3$ or $AlBr_3$ (*28*). Bestian and Clauss (*24*) report that the system CH_3TiCl_3–CH_3AlCl_2 in CH_2Cl_2 or $PhCH_3$ will polymerize ethylene at −70°C. The activity of the CH_3TiCl_3 is enhanced by the presence of CH_3AlCl_2. Both the stability and the lack of polymerization activity in the absence of other metal alkyls or halides suggest that the Ti–C bond in CH_3TiCl_3 is more stable than in the postulated $RTiCl_4$-olefin complex.

TABLE 3

ELECTRONIC ENERGY LEVELS FOR CH_3TiCl_3

Representation	Energy (eV)	Electronic configuration
$8a_1$	4.67	
$7a_1$	−4.39	
$7e$	−5.24	
$6a_1$	−5.36	
$6e$	−5.52	
$5e$	−7.66	
$5a_1$	−10.88	XX
$1a_2$	−11.63	XX
$4e$	−12.20	XXXX
$3e$	−12.70	XXXX
$4a_1$	−12.96	XX
$3a_1$	−13.44	XX
$2e$	−13.49	XXXX
$2a_1$	−21.13	XX
$1e$	−23.91	XXXX
$1a_1$	−24.5	XX
Charge on Ti		+0.54
Coulomb energies	Ti 3*d*	−10.15
	4*s*	−9.30
	4*p*	−6.04
	C 2*p*	−10.0
	2*s*	−21.0
	Cl 3*p*	−12.10
	Cl 3*s*	−23.70

The geometric configuration of CH_3TiCl_3 was assumed to be a distorted tetrahedron (symmetry C_{3V}). The arrangement and numbering of the atoms is shown in Fig. 1. The bond distance Ti–Cl was taken to be 2.18 Å, the same as in $TiCl_4$. The Ti–C bond distance was assumed to be 2.0 Å. The molecular orbitals of CH_3TiCl_3 belong to the irreducible representations A_1, A_2, and E of group C_{3V}, and are labeled accordingly in Table 3.

The orbital of symmetry A_2 is a nonbonding combination of chlorine p orbitals. The orbitals of symmetry A_1 and E contain contributions from central atom and chlorine orbitals, but only the orbitals of symmetry A_1 contain contributions from the carbon p and s orbitals. The molecular orbital energies are given in Table 3. The highest filled orbital of the bonding scheme is $5a_1$ with the first empty one being $5e$. The $5a_1$ to $5e$ transition represents a breaking of the Ti–C bond, which can best be indicated by the eigenvectors of the respective molecular orbitals. As indicated in Table 4, the $5a_1$ level contains the principal contribution to the σ bond between the carbon and titanium atoms. However, there

TABLE 4

EIGENVECTORS FOR $5a_1$ AND $5e$ LEVELS IN CH_3TiCl_3

Orbital	$5a_1$	Orbital	$5e$
Ti $3d_{z^2}$	−0.3922	Ti $3d_{xz}$	−0.8821
Ti $4s$	−0.1032	Ti $3d_{x^2-y^2}$	−0.2907
Ti $4p_z$	0.0339	Ti $4p_x$	−0.0779
C $2p_z$	0.8095	C $2p_z$	0.0000
C $2s$	0.1596	C $2s$	0.0000
Cl^1 $3s$	0.0039	Cl^1 $3s$	−0.0577
$3p_z$	−0.1359	$3p_z$	0.3823
$3p_x$	−0.1278	$3p_x$	0.3083
Cl^2 $3s$	0.0039	Cl^2 $3s$	0.0288
$3p_z$	−0.1359	$3p_z$	−0.1910
$3p_x$	0.0639	$3p_x$	−0.1134
$3p_y$	−0.1108	$3p_y$	−0.2433
Cl^3 $3s$	0.0039	Cl^3 $3s$	0.0289
$3p_z$	−0.1359	$3p_z$	−0.1912
$3p_x$	0.0639	$3p_x$	−0.1133
$3p_y$	0.1108	$3p_y$	0.2434

is no contribution to the electron density on the carbon atom in $5e$. Consequently, it is concluded that an electron transfer from $5a_1$ to $5e$ represents an initial step in the breaking of the Ti–C bond.

The calculated energy of transition from $5a_1$ to $5e$ is 3.22 eV, which is much too high for a thermal excitation. Hence, the high electronic transition for polymerization. This is in agreement with the proposal by Chatt and Shaw (*25*) which relates the strength of metal-to-carbon bonds with the energy gap between the highest filled and lowest empty or half-filled orbital.

V. ELECTRONIC STRUCTURE FOR $RTiCl_4$ AND $RTiCl_4$-OLEFIN POLYMERIZATION COMPLEX

Cossee suggested an octahedral configuration (Fig. 2) for the active center in a $TiCl_3$-aluminum alkyl catalyst. With this configuration, a transition metal–alkyl bond and an olefin coordination site are properly positioned for the propagation step via an insertion reaction. Since the catalyst system can be stored for a practically indefinite time, Cossee suggested that the Ti–C bond in the $RTiCl_4$ complex must be relatively stable in the absence of unsaturated hydrocarbons. Calculations of the energy levels in this complex support Cossee's suggestion.

The interatomic distances in the complex were assumed to be as follows: Ti–Cl, 2.35 and Ti–C, 2.0. The Ti–Cl bond distance is equal to the distance reported for $TiCl_6^{2-}$ (*26*). Table 5 contains the electronic levels in the complex. The states of $RTiCl_4$ are in C_s symmetry and the two irreducible representations of the group are used to identify the various one-electron levels in Table 5. A value of −8.72 eV, minus the ionization potential for the ethyl radical, was used in these calculations for the Coulomb energy of the carbon $2p$ orbital. For the carbon s orbital, the Coulomb energy of −21.0 eV was used in all calculations. The highest filled orbital ($12a'$) in the bonding scheme of $RTiCl_4$ represents a bond between the alkyl group and the titanium atom. This bonding is best shown by the eigenvectors for the molecular orbital. The eigenvectors for $12a'$ and the half-filled orbital, $13a'$, are presented in Table 6. For the $12a'$ orbital, the coefficient on the carbon $2p_z$ orbital is 0.8471 and 0.0885 on the carbon s orbital with fairly large coefficients on the Ti $3d_{z^2}$, $3d_{yz}$, and $4s$ orbitals. There is also some mixing of the chlorine $3p_z$ orbitals. The large coefficients for the carbon and titanium orbitals indicate a significant contribution to the electron density on these atoms. With the orbitals in a bonding combination, the carbon is bonded to the metal atom. In the

TABLE 5

ELECTRONIC ENERGY LEVELS IN $RTiCl_4$

Irreducible representation	Energy level (eV)	Electronic configuration
$18a'$	7.52	
$17a'$	−1.33	
$16a'$	−4.62	
$9a''$	−4.75	
$15a'$	−4.97	
$14a'$	−5.91	
$8a''$	−7.59	
$7a''$	−7.62	
$13a'$	−8.15	X
$12a'$	−9.22	XX
$6a''$	−11.03	XX
$5a''$	−11.24	XX
$11a'$	−11.43	XX
$10a'$	−11.73	XX
$9a'$	−11.88	XX
$4a''$	−12.25	XX
$8a'$	−12.50	XX
$7a'$	−12.75	XX
$6a'$	−13.07	XX
$3a''$	−13.33	XX
$2a''$	−13.51	XX
$5a'$	−13.67	XX
$4a'$	−20.91	XX
$3a'$	−23.59	XX
$2a'$	−23.95	XX
$1a''$	−24.38	XX
$1a'$	−25.50	XX
Charges on Ti		+0.57
Coulomb energies	$3d$	−9.46
	$4s$	−8.84
	$4p$	−5.58
	C $2p_z$	−8.72
	$2s$	−21.0
	C $2p_y$	−9.70
	Cl $3p$	−12.10
	$3s$	−23.70

13*a*′ molecular orbital, there is very little mixing of the $2p_z$ orbital, as indicated by a coefficient of 0.0642. Consequently, an electron transfer from 12*a*′ to 13*a*′ represents in effect an initial step in the breaking of the Ti–C bond. The energy of this transition is 1.07 eV, which means that the complex should be fairly stable as hypothesized by Cossee.

TABLE 6

Eigenvectors for Molecular Orbitals 12*a*′ and 13*a*′ in the $RTiCl_4$ Complex

Orbital	Eigenvector	
	12*a*′	13*a*′
Ti $3d_z{}^2$	*−0.3006*	*−0.0573*
$3d_{x^2-y^2}$	0.0071	−0.0572
3*dyz*	−0.1043	*0.9595*
4*s*	−0.0925	0.0206
$4p_z$	0.0846	0.0544
$4p_y$	−0.0045	0.0512
C $2p_z$	*0.8471*	*0.0642*
C 2*s*	0.0885	−0.0153
Cl^1 $3p_z$	0.1050	−0.0083
$3p_x$	−0.0011	−0.0044
$3p_y$	0.0050	−0.0275
3*s*	−0.0017	0.0005
Cl^4 $3p_z$	0.0532	0.3742
$3p_y$	0.0003	−0.0219
3*s*	−0.0014	−0.0067
Cl^2 $3p_z$	0.1050	−0.0083
$3p_x$	0.0011	0.0044
$3p_y$	0.0050	0.0275
3*s*	−0.0017	0.0005
Cl^3 $3p_z$	0.3253	0.0651
$3p_y$	−0.0691	0.3519
3*s*	0.0953	0.0219

When the olefin is coordinated with the titanium at the vacant octahedral site of the $RTiCl_4$ complex, the 2*p* orbitals of the olefin mix primarily with the d_{yz} and $d_z{}^2$ orbitals to lower the energy of transition between the highest filled orbital and the orbital above this level, which is half-filled. The electronic energy levels for the catalyst-olefin complex are presented in Table 7. For the two levels of particular interest, 13*a*′ and 14*a*′, the eigenvectors are given in Table 8. In state 13*a*′, the coefficients on the alkyl-carbon $2p_z$ and 2*s* orbitals are 0.7278 and 0.1071, but are decreased to 0.3661 and 0.0021, respectively, in the 14*a*′ state. There is a corresponding increase in the coefficient on the $3d_{yz}$ orbital of titanium. The transition from 13*a*′ to 14*a*′ therefore represents a transfer of electron density from the alkyl group to the Ti atom which weakens the Ti–C bond. Also, in state 14*a*′, the alkyl

TABLE 7

Electronic Energy Levels in $RTiCl_4$-Olefin Complex

Irreducible representation	Energy level (eV)	Electronic configuration
20*a*′	3.66	
19*a*′	−1.72	
18*a*′	−2.90	
17*a*′	−4.45	
16*a*′	−4.68	
9*a*″	−4.87	
15*a*′	−5.55	
8*a*″	−7.64	
7*a*″	−7.67	
14*a*′	−8.74	X
13*a*′	−9.40	XX
6*a*″	−11.05	XX
12*a*′	−11.24	XX
5*a*″	−11.25	XX
11*a*′	−11.53	XX
10*a*′	−11.72	XX
9*a*′	−12.24	XX
8*a*′	−12.31	XX
4*a*″	−12.48	XX
7*a*′	−12.77	XX
3*a*″	−13.22	XX
6*a*′	−13.27	XX
2*a*″	−13.45	XX
5*a*′	−13.82	XX
4*a*′	−20.96	XX
3*a*′	−23.56	XX
2*a*′	−23.86	XX
1*a*″	−24.21	XX
1*a*′	−25.17	XX
Charge on Ti		+0.56
Coulomb energies	Ti 3*d*	−9.38
	4*s*	−8.78
	4*p*	−5.53
	C′ 2*p*	−8.72
	2*s*	−21.0
	C^2 2*p*	−9.7
	C^3 2*p*	−9.7
	Cl 3*p*	−12.10
	3*s*	−23.70

carbon $2p_z$ and $2s$ orbitals are in a bonding combination with the olefin $2p_y$ orbital. Consequently, the initial step in the insertion reaction has been accomplished by one-electron transition from the ground state of the complex. In terms of energy, the $13a'$ to $14a'$ transition in Table 7 is 15.2 kcal/mole, which is near the experimental activation energies of 10–14 kcal/mole reported in the literature.

TABLE 8
EIGENVECTORS FOR MOLECULAR ORBITALS $13a'$ AND $14a'$ IN $RTiCl_4$-OLEFIN COMPLEX

Orbital	Eigenvector	
	$13a'$	$14a'$
Ti $3d_z{}^2$	*−0.3206*	−0.1598
$3d_{x^2-y^2}$	−0.0466	−0.0264
$3dyz$	−0.3155	*0.7502*
$4s$	−0.0733	−0.0343
$4p_z$	0.0671	0.0676
$4p_y$	−0.0280	0.0360
C^1 $2p_z$	*0.7278*	*0.3661*
$2s$	0.1071	0.0021
C^2 $2p_y$	0.0875	−0.2068
C^3 $2p_y$	−0.2759	0.2479
Cl^1 $3p_z$	0.1006	0.0179
$3p_x$	−0.0033	0.0018
$3p_y$	−0.0140	−0.0194
$3s$	−0.0015	0.0003
Cl^4 $3p_z$	−0.0482	0.3414
$3p_y$	−0.0886	0.0092
$3s$	−0.0222	0.0030
Cl^2 $3p_z$	0.1006	0.0179
$3p_x$	0.0033	−0.0018
$3p_y$	−0.0140	−0.0194
$3s$	−0.0015	−0.0003
Cl^3 $3p_z$	0.2177	0.2381
$3p_y$	−0.2554	0.3466
$3s$	0.0594	0.0645

This result was obtained using the interatomic distances indicated in Fig. 2 with a value of −8.72 eV for the Coulomb energy of the alkyl $2p_z$ orbital and −9.70 eV for the Coulomb energy of the olefin $2p_y$ orbitals. If the interatomic distances are expanded to the values suggested by Cossee, i.e., Ti–Cl, 2.55; Ti–R, 2.75; Ti–CC, 2.55; and C–C, 1.7; the transition becomes 0.36 eV or 8.3 kcal/mole, which is slightly below the range of the reported activation energy.

VI. CONCLUSIONS

(1) The energy of the lowest electronic transition in the catalyst complex, $RTiCl_4$-olefin, was calculated to be near the activation energy (10–14 kcal/mole) of the polymerization reaction. This transition is a transfer of electron density which corresponds to an initial step in an olefin insertion reaction as suggested by others.

(2) The electronic energy levels in $RTiCl_4$ and CH_3TiCl_3 were used to judge the relative stability of these complexes. For both, the electronic transition which corresponds to an initial step in the breaking of the Ti–C bond was found to be high enough to indicate stability which is in accordance with experimental evidence.

(3) The results of this study clearly indicate that the IBM computer program based on molecular orbital methods can be used to examine the electronic structure of the chemical intermediates in catalytic reactions.

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