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An Intermolecular Perturbation Approach to the Cycloaddition of Carbenes toward Olefins. Reaction Path and Stereoselectivity

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The perturbation theory of Murrell, Randić and Williams for intermolecular interaction has been combined with the assumption of local zero-differential overlaps. The theory has been applied to the cycloadditions of singlet methylene and halocarbenes toward olefins. The results, obtained by use of the CNDO/2 energies and wave functions for isolated molecules, quantitatively assess the roles of various types of energies influencing the stereochemical courses of reaction. The syn/anti stereoselectivities of halocarbenes in their cycloadditions toward *cis*-butene-2 are found to be governed by the Coulombic, dispersion, charge-transfer and exchange-repulsion energies altogether. Participation of the *d* orbitals of the chlorine atom in charge transfer is emphasized.

Die Störungsrechnung von Murrell, Randić und Williams für intermolekulare Wechselwirkung wurde in Verbindung mit der Annahme von lokalen ZDO zur Berechnung der Cycloaddition von Singulett-Methylen oder -Halogencarbenen an Olefine angewendet. Die Resultate, die über die CNDO/2-Ergebnisse für die isolierten Moleküle erhalten wurden, lassen die Rolle der einzelnen Energieanteile erkennen, die die Stereochemie der Reaktion beeinflussen. Die syn/anti-Stereoselektivität der Halogencarbene gegenüber *cis*-2-Buten wird durch die Coulomb-, Dispersions-, Charge-transfer- und Austausch-Wechselwirkung gemeinsam bestimmt. Auch die D-Orbitale von Chlor sind für den Charge transfer von Bedeutung.

Introduction

The cycloaddition of singlet carbenes toward olefins has been the subject of intensive investigation in organic chemistry for the past ten years [1]. Studies on the stereochemical details of the reaction have yielded valuable informations concerning the chemical properties of singlet carbene intermediates. It is generally accepted that at the incipient stage of reaction they interact with both the olefin carbons in a concerted manner, to give cyclopropanes with the initial olefin configuration (*cis* or *trans*) retained perfectly.

It is also well recognized that unsymmetrically substituted carbenes show, in addition to the above-mentioned stereospecificity, a definite pattern of stereoselection as to the placement of their substituent(s) in the products. Thus, bulkier substituents of carbene tend to be imbedded at a position *cis* to the larger number of olefin substituents [1–3]. The formations of presumably thermodynamically less stable syn isomers in prevalence over the anti isomers clearly reflect the operation of electronic attractive forces outweighing steric repulsion between the carbene and olefin substituents in the transition state. Nonetheless, the precise nature of these intermolecular forces is still a moot point; apparently, little effort has been expended on theoretical studies of this problem.

The primary purpose of this paper is to attempt an intermolecular-interaction approach to the syn/anti stereoselectivity of halocarbenes. To this end, the intermolecular perturbation theory of Murrell *et al.* [4] was used, in combination with the CNDO wave functions and energies [5–7] of the reacting partners. For assumed geometries of the reacting systems, various types of interaction energies, i.e., the Coulomb, exchange-repulsion, induction, dispersion and charge-transfer energies, were evaluated separately, and their relative importances to stereoselectivity were assessed. The results were found to be of value to the understanding of the stereochemistry of the carbene intermediates.

Theory and Calculation Method

It is presumed that for the interaction systems of our present interest the effect of the orbital overlaps between the components is significant. For treatments of such systems, the intermolecular perturbation theory presented by Murrell *et al.* [4] is a particularly suited starting point.

Let us denote the component closed-shell molecules by A and B. The theory of Murrell *et al.* is essentially the configuration interaction treatment, in which the locally excited (A^*B and AB^*), doubly excited (A^*B^*) and charge-transfer (A^+B^- and A^-B^+) configurations of the aggregate are allowed to mix with the ground-state configuration (AB). The wave function of each configuration was antisymmetrized with respect to electron exchange between the components. Under this requirement, they calculated the stabilization energy of the ground state due to the configuration interaction, by a double perturbation expansion with respect to the intermolecular potential U and overlap S up to the order of U^2S^2. General expressions for the Coulombic (U^1S^0), exchange-repulsion (U^1S^2), induction-dispersion (U^2S^0) and charge-transfer (U^2S^2) energies were thus derived.

We further expand each of these general expressions into terms associated with atomic orbitals, χ. For the sake of computational economy, we decided to adopt the assumption of zero-differential overlaps [5] within molecules but retain the overlaps between the interacting molecules. The intermolecular atomic-orbital integrals required to consider are the electron-core attraction, interelectronic repulsion, and atomic overlap integrals of the form:

$$V_{a,rs} = -\int \chi_r(1) \frac{Z_a e^2}{r_{1a}} \chi_s(1)\, d\tau_1\,, \tag{1}$$

$$(rs|tu) = \int \chi_r(1)\, \chi_s(1) \frac{e^2}{r_{12}} \chi_t(2)\, \chi_u(2)\, d\tau_1\, d\tau_2\,, \tag{2}$$

and

$$S_{rs} = \int \chi_r(1)\, \chi_s(1)\, d\tau_1 \tag{3}$$

respectively, where the suffix a signifies atomic core while r, s, t and u, valence-shell atomic orbitals.

Expansions were somewhat tedious but straightforward. The final forms obtained for the Coulombic (E_Q), exchange-repulsion (E_K), induction (E_I), dispersion (E_D) and charge-transfer (E_{CT}) energies were as follows:

$$\begin{aligned} E_Q = {} & \sum_{r}^{\mathrm{A}}\sum_{b}^{\mathrm{B}} P_{rr} V_{b,rr} + \sum_{s}^{\mathrm{B}}\sum_{a}^{\mathrm{A}} P_{ss} V_{a,ss} \\ & + \sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} P_{rr} P_{ss} (rr|ss) + \sum_{a}^{\mathrm{A}}\sum_{b}^{\mathrm{B}} Z_a Z_b e^2/R_{ab}\,, \end{aligned} \tag{4}$$

$$\begin{aligned} E_K = {} & -\frac{1}{2}\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}}\sum_{t}^{\mathrm{A}}\sum_{u}^{\mathrm{B}} P_{rt} P_{su} (rs|tu) \\ & -2\sum_{i}^{\mathrm{A}}\sum_{j}^{\mathrm{B}}\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}}\sum_{a}^{\mathrm{A}}\sum_{b}^{\mathrm{B}} S_{ij} C_{ir} C_{js} (V_{a,rs} + V_{b,rs}) \\ & -2\sum_{i}^{\mathrm{A}}\sum_{j}^{\mathrm{B}}\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} S_{ij} C_{ir} C_{js} \left\{\sum_{t}^{\mathrm{A}} (P_{tt} - C_{it}^2)(rs|tt) + \sum_{u}^{\mathrm{B}} (P_{uu} - C_{ju}^2)(rs|uu)\right\} \\ & +2\sum_{i}^{\mathrm{A}}\sum_{j}^{\mathrm{B}} S_{ij}^2 \left\{\sum_{r}^{\mathrm{A}}\sum_{b}^{\mathrm{B}} C_{ir}^2 V_{b,rr} + \sum_{s}^{\mathrm{B}}\sum_{a}^{\mathrm{A}} C_{js}^2 V_{a,ss}\right\} \\ & +2\sum_{i}^{\mathrm{A}}\sum_{j}^{\mathrm{B}}\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} S_{ij}^2 (P_{rr} C_{js}^2 + P_{ss} C_{ir}^2 - C_{ir}^2 C_{js}^2)(rr|ss)\,, \end{aligned} \tag{5}$$

$$\begin{aligned} E_I = {} & 2\sum_{i}^{\mathrm{A}}\sum_{k}^{\mathrm{A}} \left\{\sum_{r}^{\mathrm{A}} C_{ir} C_{kr} \left[\sum_{b}^{\mathrm{B}} V_{b,rr} + \sum_{s}^{\mathrm{B}} P_{ss}(rr|ss)\right]\right\}^2 \Big/ (E_0 - E_{i\to k}) \\ & +2\sum_{j}^{\mathrm{B}}\sum_{l}^{\mathrm{B}} \left\{\sum_{s}^{\mathrm{B}} C_{js} C_{ls} \left[\sum_{a}^{\mathrm{A}} V_{a,ss} + \sum_{r}^{\mathrm{A}} P_{rr}(rr|ss)\right]\right\}^2 \Big/ (E_0 - E_{j\to l})\,, \end{aligned} \tag{6}$$

$$E_D = 4\sum_{i}^{\mathrm{A}}\sum_{k}^{\mathrm{A}}\sum_{j}^{\mathrm{B}}\sum_{l}^{\mathrm{B}} \left\{\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} C_{ir} C_{kr} C_{js} C_{ls} (rr|ss)\right\}^2 \Big/ (E_0 - E_{i\to k, j\to l})\,, \tag{7}$$

$$\begin{aligned} E_{CT} = {} & 2\sum_{i}^{\mathrm{A}}\sum_{l}^{\mathrm{B}} \left\{\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} C_{ir} C_{ls} \left[\sum_{b}^{\mathrm{B}} V_{b,rs} + \sum_{u}^{\mathrm{B}} P_{uu}(rs|uu)\right]\right. \\ & \left. - S_{ij} \sum_{r}^{\mathrm{A}} C_{ir}^2 \left[\sum_{b}^{\mathrm{B}} V_{b,rr} + \sum_{s}^{\mathrm{B}} P_{ss}(rr|ss)\right]\right\}^2 \Big/ (E_0 - E_{i\to l}) \\ & +2\sum_{k}^{\mathrm{A}}\sum_{j}^{\mathrm{B}} \left\{\sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} C_{kr} C_{js} \left[\sum_{a}^{\mathrm{A}} V_{a,rs} + \sum_{t}^{\mathrm{A}} P_{tt}(rs|tt)\right]\right. \\ & \left. - S_{ij} \sum_{s}^{\mathrm{B}} C_{js}^2 \left[\sum_{a}^{\mathrm{A}} V_{a,ss} + \sum_{r}^{\mathrm{A}} P_{rr}(rr|ss)\right]\right\}^2 \Big/ (E_0 - E_{j\to k})\,. \end{aligned} \tag{8}$$

In Eqs. (4) through (8), we have used the following notations for molecule A (and B in parentheses): i (and j), the occupied molecular orbital; k (and l), the unoccupied virtual molecular orbital; r, t (and s, u), the atomic orbitals involved; and a (and b), the atomic core present. In addition, C_{ir} etc. and P_{rr} etc. respectively denote the LCAO coefficients and atomic-orbital populations for the isolated molecule, and S_{ij} signifies the intermolecular orbital overlap.

$$S_{ij} = \sum_{r}^{\mathrm{A}}\sum_{s}^{\mathrm{B}} C_{ir} C_{js} S_{rs}\,. \tag{9}$$

E_0 is the electronic energy of the ground configuration AB while $E_{i \to k}$ etc. are the energies of the configurations resulting from the electron transitions indicated. R_{ab} is the distance between atomic cores a and b.

In evaluating the various energies (4)–(8) numerically, we made use of the CNDO/2 wave functions and orbital energies [6, 7] for the interacting components. For chlorocarbenes, both of those obtained with and without inclusion of the chlorine $3d$ orbitals were used. The one- and two-electron integrals involving intermolecular differential overlaps were approximated by Mulliken's formula [8], viz.,

$$V_{a,rs} = (V_{a,rr} + V_{a,ss})\, S_{rs}/2 \tag{10}$$

and

$$(rs|tu) = \{(rr|tt) + (rr|uu) + (ss|tt) + (ss|uu)\}\, S_{rs} S_{tu}/4\,. \tag{11}$$

The integrals, $V_{a,rr}$, $(rr|rr)$ and $(rr|ss)$, were evaluated for the Slater valence-shell s atomic orbitals [9]. The overlap integrals S_{rs} were also evaluated for Slater orbitals, using the formula given by Mulliken *et al.* [10].

Molecular geometries of ethylene [11], *cis*-butene [12], methylene [13], fluorocarbene [14] were obtained from the literature. The geometries for fluorochlorocarbene ($\sphericalangle$FCCl = 103°) and methylchlorocarbene ($\sphericalangle$CCCl = 106°) were estimated by reference to those reported for chlorocarbene [15]. The interaction energies were computed for several assumed spatial geometries of the aggregates AB. All computations were programed in FORTRAN and performed on the FACOM 230-60 at the Kyoto University Computation Center. The CNDO/2 wave functions were required to be precise to within 0.0001 for the charge densities obtained.

Additions of Methylene

Before dealing with stereoselectivity, we consider in this section the additions of singlet methylene $CH_2(^1A_1)$ toward ethylene and *cis*-butene-2. Examination of the geometry of the transition states is the main purpose.

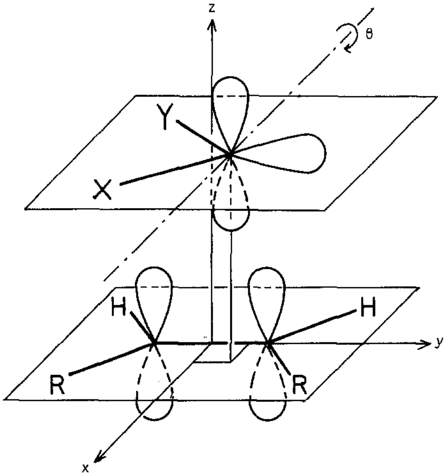

Fig. 1. Coordinate axes chosen for the interacting system. The spatial arrangement of carbene relative to olefin is illustrated for the syn-X π-approach ($\theta = 0°$)

We consider various spatial geometries of CH_2 relative to olefin, each component retaining its initial planar structure. Fig. 1 illustrates such geometries. The middle of the olefin double bond is taken as the origin of the Cartesian coordinates, x, y and z. The methylene plane was allowed to rotate around the auxiliary axis which passes through the carbon atom and is parallel to the x axis. The nodal axis of the methylene lone pair orbital was fixed to be parallel to the yz plane, and its declination downward was defined as the rotation angle θ of methylene. Thus, the geometry of the entire system is characterized by the notation (x, y, z, θ) in units of Å and degree.

1. Addition to Ethylene

In the first place, methylene was assumed to approach ethylene along the z-axis. Two extreme geometries were considered: $\theta = 0$ and 90°, which may be referred to as the π- and σ-approach models, respectively. The various types of energies, given by Eqs. (4)–(8), were calculated for the varying intermolecular distance z. The results are summarized in Table 1.

Table 1 shows that, as the intermolecular distance decreases, the π-approach tends to be stabilized increasingly whereas the σ-approach suffers increasing destabilization. The main contribution to the stability of the former model is E_{CT}, while in the latter the stabilization due to E_{CT} is overshadowed by the destabilization arising from exchange repulsion E_K. These results are compatible with Hoffmann's demonstration [16] based on the total energy calculations by the extended Hückel method, and are well consistent with the Woodward-Hoffmann selection rule for thermal cycloadditions [17].

Next, we calculated the interaction energies for two π-approach models: $B(0, -0.3, 3.2, 0)$ and $C(0, 0.3, 3.2, 0)$. The displacements $y = \pm 0.3$ Å correspond to about one-fourth the length of the double bond, while the separation $z = 3.2$ Å is approximately twice the van der Waals radius of the carbon $p\pi$ orbital [18].

Table 1. Energies of interaction between CH_2 and ethylene[a]

z (Å)	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
σ-approach ($\theta = 90°$)						
2.8	−0.985	3.440	−0.000	−0.112	−0.723	1.619
3.2	−0.171	0.822	−0.000	−0.056	−0.166	0.430
3.6	−0.027	0.177	−0.000	−0.030	−0.035	0.086
4.0	−0.004	0.035	−0.000	−0.017	−0.007	0.008
5.0	−0.000	0.000	−0.000	−0.005	−0.000	−0.005
π-approach ($\theta = 0°$)						
2.8	−1.205	2.449	−0.001	−0.292	−6.844	−5.892
3.2	−0.217	0.582	−0.000	−0.151	−1.627	−1.413
3.6	−0.037	0.128	−0.000	−0.083	−0.348	−0.340
4.0	−0.006	0.027	−0.000	−0.048	−0.069	−0.096
5.0	−0.000	0.000	−0.000	−0.014	−0.001	−0.015

[a] Energies given in units of kcal/mole. Geometry: $x = y = 0$ Å.

Table 2. Interaction energies for π-approaches of CH_2 toward ethylene and *cis*-butene-1[a]

Geometry (x, y)[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
Ethylene						
$A(0, 0)$	−0.217	0.582	−0.000	−0.151	−1.627	−1.413
$B(0, -0.3)$	−0.210	0.543	−0.000	−0.134	−1.577	−1.377
$C(0, 0.3)$	−0.218	0.596	−0.000	−0.161	−1.571	−1.353
cis-Butene-2						
$A(0, 0)$	−0.284	0.816	−0.000	−0.260	−1.553	−1.281
$B(0, -0.3)$	−0.308	0.860	−0.000	−0.252	−1.547	−1.246
$C(0, 0.3)$	−0.276	0.773	−0.000	−0.265	−1.530	−1.299
$D(-0.3, 0)$	−0.253	0.716	−0.000	−0.242	−1.485	−1.264
$E(0.3, 0)$	−0.296	0.860	−0.000	−0.269	−1.504	−1.209

[a] Energies given in units of kcal/mole.

[b] $z = 3.2$ Å and $\theta = 0°$.

The results of calculation are given in Table 2, together with those for Model $A(0, 0, 3.2, 0)$. The total stability is found to decrease in the order of $A > B > C$. From his extended Hückel calculations, Hoffmann [16] pointed out that a π-approach which is slightly off-centered toward the position C would be favorable as a result of steric interactions between hydrogens. Our results conflict with his view. The repulsions between the lone pair electrons of methylene and the π-electrons of ethylene appears to be greater than those between the hydrogens.

2. *Addition to cis-Butene-2*

The various types of interaction energies were calculated as the functions of θ for fixed coordinates $x = y = 0$ and $z = 3.2$ Å. The results obtained are shown in Fig. 2.

As can be seen in Fig. 2, the total interaction energy E_{total} is determined almost exclusively from two opposing contributions, E_{CT} and E_K. E_{CT} is a sensitive function of θ and attains a minimum (the largest negative value) at $\theta = 0°$, as is easily anticipated. By contrast, E_K takes on a minimal value at $\theta = 30°$, an angle which probably permits the best compromise between the steric crowdings associated with the hydrogen atoms of methylene on one hand and its lone pair electrons on the other. As a consequence, E_{total} first decreases with the increase in θ, giving a shallow minimum at $\theta = 10°$, beyond which it sharply increases. The π-approach model ($\theta = 0°$) can thus be regarded as a useful approximation to the present interaction system.

With the above indications in mind, we next looked into differential responses of the system to slight changes in x and y. For fixed values of $z = 3.2$ Å and $\theta = 0°$, we considered the following five geometries: $A(0, 0, 3.2, 0)$, $B(0, -0.3, 3.2, 0)$, $C(0, 0.3, 3.2, 0)$, $D(-0.3, 0, 3.2, 0)$ and $E(0.3, 0, 3.2, 0)$. Fig. 3 is the top view of the whole system, illustrating the locations of the carbene carbon in the geometries A to E.

The interaction energies calculated for the five geometries are given in Table 2. The most important stabilizing factor is E_{CT}. The relative stability of the system

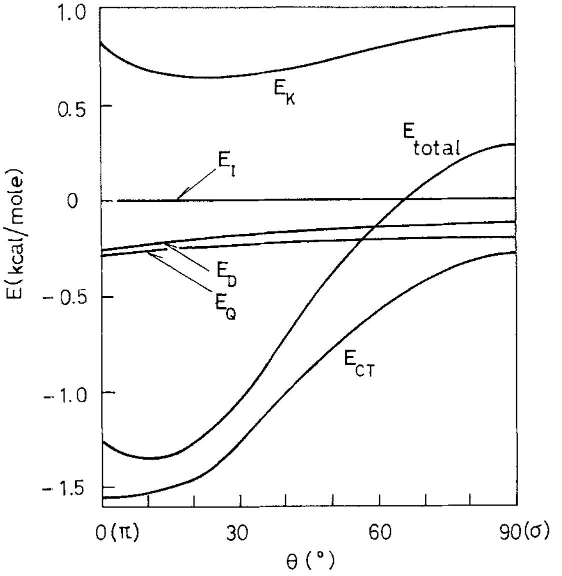

Fig. 2. Angular dependences of various types of interaction energies for the CH_2-*cis*-butene system

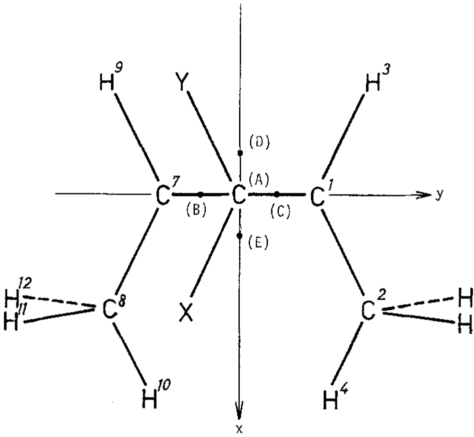

Fig. 3. Projection of CXY on the *cis*-butene-2 plane. The symbols (*A*), (*B*), (*C*), (*D*) and (*E*) indicate the projected positions of the carbene carbon atom. The numbers 1–12 are the atom numberings for *cis*-butene-2

decreases in the order of $C > A > D > B > E$. The relative instabilities of *B* and *E* are primarily due to the repulsion term E_K, which is large because of the close proximity of a methylene hydrogen atom to the methyl group of butene. It is of interest to note that, unlike the case of ethylene, *C* is more stable than *A*, indicative of the large repulsive forces associated with the methyl group.

As a summary for this section, one may state that the stabilities of the incipient methylene-olefin aggregates are determined primarily by the balancings between the two opposing contributions, E_{CT} and E_K. The π-approach along the z-axis would not be a very unlikely reaction path. E_Q is unimportant, as it should be for systems comprising non-polar molecules. Neither is E_D relatively important, except for large intermolecular separations. E_I is extremely small and thus can be neglected.

Stereoselectivity of Halocarbenes

Calculations analogous to those described in the preceding section have been carried out for the additions of some halocarbenes toward *cis*-butene-2. The halocarbenes treated are fluorocarbene (CHF), fluorochlorocarbene (CFCl) and methylchlorocarbene (CH_3CCl). The specific purpose is to compare the relative eases of the two stereo-courses leading to the formations of syn and anti cycloadducts (Fig. 1).

1. CHF

Free fluorocarbene generated by the thermolysis of fluorodiazomethane is known to be least stereoselective, giving an approximately 1 : 1 mixture of syn and anti addition products with *cis*-butene-2 [19]. Nonetheless, it will be theoretically of interest to diagnose its intrinsic character in the interaction.

The energies of interaction between CHF and *cis*-butene-2 were calculated for the syn-F and anti-F π-approach models at the interplanar distances $z = 2.8$, 3.2 and 3.7 Å. Table 3 summarizes the results obtained for the cases in which both x and y were assumed to be 0.

It can be seen in Table 3 that at every distance studied the total stabilization energy ($-E_{\text{total}}$) is slightly greater for the syn-F orientation. At the greatest distance studied (3.7 Å), E_D and E_{CT} are of dominant importance to the stability of the system. However, the factors which tend to lead the F atom to the syn orientation are E_Q, E_K and E_D. As the distance diminishes, E_K and E_{CT} increase in magnitude far more rapidly than do the remaining energies. This is because E_K and E_{CT} involve a greater overlap dependence (S^2) as compared with the rest. To the selection of the syn-F orientation, however, E_Q and E_D would also make some contribution. At $z = 2.8$ Å, contributions of the four types of energies are almost equally important.

Small changes in x, y and θ did not alter the results materially. The overall situations were much the same as those delineated for the methylene-*cis*-butene system. In what follows, we will treat problems with the carbon atom of carbenes fixed at a point where $x = y = 0$ and $z = 3.2$ Å.

Table 3. Stereoselectivity of CHF in the addition toward *cis*-butene-2[a]

z(Å)	Configuration[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
2.8	syn	−1.539	3.203	−0.021	−0.646	−5.479	−4.482
	anti	−1.365	3.179	−0.015	−0.566	−5.227	−3.994
3.2	syn	−0.311	0.744	−0.012	−0.352	−1.336	−1.266
	anti	−0.255	0.774	−0.008	−0.312	−1.303	−1.104
3.7	syn	−0.055	0.110	−0.006	−0.175	−0.200	−0.327
	anti	−0.022	0.122	−0.004	−0.158	−0.202	−0.265

[a] Energies given in units of kcal/mole. Geometry: $x = y = 0$ Å and $\theta = 0°$.

[b] With respect to the F atom.

2. CFCl

Fluorochlorocarbene produced by the action of potassium *t*-butoxide on sym-tetrachlorodifluoroacetone is reported to add to *cis*-butene-2 in the syn-Cl/anti-Cl ratio of 2.40 [20]. The greater syn selectivity of the chlorine atom as compared with the fluorine atom has been interpreted as being due to the greater electrostatic attraction of the more polarizable chlorine atom [20]. It is implicit that this stabilizing effect overcomes the differential in the adverse steric effects of the halogens.

Results of our calculation are interesting in connection with the above-mentioned qualitative view. As will be described below, the sum of the attractive interaction energies is certainly greater in magnitude for the syn-Cl orientation but that it cannot offset the disadvantage arising from the repulsion energy unless the 3*d* vacant orbitals of the chlorine atom is taken into consideration.

Because of the bulkiness of the chlorine atom, the π-approach can hardly be satisfactory approximation. Thus, the rotation angle which minimizes E_{total} for the syn-Cl orientation was searched. It was found to be ca. 20°. Table 4 lists the results of calculation for three cases: (1) $\theta = 0°$ without the *d* orbitals; (2) $\theta = 20°$ without the *d* orbitals; and (3) $\theta = 20°$ with the *d* orbitals included.

For both Cases 1 and 2, the syn-Cl orientation is calculated to be the less stable. In Case 1, the relative instability of the syn orientation is due to its outstandingly large value of E_K. In Case 2, this repulsion is reduced considerably at a slight sacrifice of E_{CT}. In the meanwhile, the anti-Cl orientation gains extra stability through E_Q. The net result is that the anti-Cl form is still the more stable. In Case 3, uniquely among the three cases studied, the syn-Cl orientation is predicted to be more stable than the anti-Cl, in agreement with observation. Clearly, this is due to a significant decrease in E_{CT} for the syn-Cl form. Both forms are more stabilized than in Case 2, primarily as a consequence of the decrease in

Table 4. Stereoselectivities of CFCl and CH_3CCl in the addition toward cis-butene-2[a]

Basis set	θ(°)	Configuration[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
CFCl								
sp	0	syn	−2.014	2.242	−0.028	−0.607	−1.403	−1.809
		anti	−1.237	1.056	−0.028	−0.496	−1.183	−1.888
sp	20	syn	−1.978	1.040	−0.019	−0.423	−1.239	−2.618
		anti	−1.947	0.719	−0.020	−0.365	−1.214	−2.827
spd	20	syn	−2.403	1.048	−0.015	−0.480	−1.916	−3.766
		anti	−2.567	0.736	−0.013	−0.395	−1.316	−3.555
CH_3CCl								
sp	20	syn	−1.464	1.312	−0.011	−0.622	−1.125	−1.910
		anti	0.396	2.288	−0.018	−0.876	−1.441	0.349
spd	20	syn	−1.468	1.322	−0.013	−0.704	−1.760	−2.623
		anti	0.404	2.312	−0.024	−0.926	−1.556	0.211

[a] Energies given in units of kcal/mole. Geometry: $x = y = 0$ Å and $z = 3.2$ Å.

[b] With respect to the Cl atom.

E_Q. The E_Q term appears to favor the anti-Cl orientation, which is, however, immaterial to the overall stereoselectivity.

The possibility that a *d*-orbital of second-row elements importantly participates in charge transfer was first pointed out by Schöllkopf *et al.* [21] in order to account for the syn selectivity of phenylthiocarbene (or, more strictly, its carbenoid). However, the type of such interactions still remains to be characterized. Thus, by analyzing the E_{CT} term for the CFCl-*cis*-butene system, we were able to verify that the interaction between the lowest vacant molecular orbital ϕ_{lv} of CFCl and the highest occupied orbital ψ_{ho} of the butene constitutes the most dominant contribution. Both these oribtals are predominantly of the π-type. Importantly, the inclusion of the chlorine *d* orbitals in the basis set greatly lowers the lowest vacant level of CFCl, thus facilitating the inter-orbital interaction mentioned above. The energies ε and wave functions of these orbitals were as follows (for the coordinate axes and atom numberings, see Fig. 3 with X=Cl and Y=F):

CFCl(*sp*):

$$\begin{aligned}\phi_{lv} &= 0.9204\,\chi(\mathrm{C}, p_z) - 0.2936\,\chi(\mathrm{F}, p_z) - 0.2582\,\chi(\mathrm{Cl}, p_z)\\ \varepsilon_{lv} &= 2.0711\ \mathrm{eV}\,.\end{aligned} \tag{12}$$

CFCl(*spd*):

$$\begin{aligned}\phi_{lv} &= 0.7960\,\chi(\mathrm{C}, p_z) - 0.2810\,\chi(\mathrm{F}, p_z) - 0.3019\,\chi(\mathrm{Cl}, p_z)\\ &\quad - 0.3403\,\chi(\mathrm{Cl}, d_{xz}) + 0.2837\,\chi(\mathrm{Cl}, d_{yz})\\ \varepsilon_{lv} &= 0.6702\ \mathrm{eV}\,.\end{aligned} \tag{13}$$

cis-Butene-2:

$$\begin{aligned}\psi_{ho} &= 0.5709\,[\chi(\mathrm{C}_1, p_z) + \chi(\mathrm{C}_7, p_z)] - 0.2228\,[\chi(\mathrm{C}_2, p_z) + \chi(\mathrm{C}_8, p_z)]\\ &\quad - 0.2494\,[\chi(\mathrm{H}_5, s) - \chi(\mathrm{H}_6, s) + \chi(\mathrm{H}_{11}, s) - \chi(\mathrm{H}_{12}, s)]\\ \varepsilon_{ho} &= -12.9075\ \mathrm{eV}\,.\end{aligned} \tag{14}$$

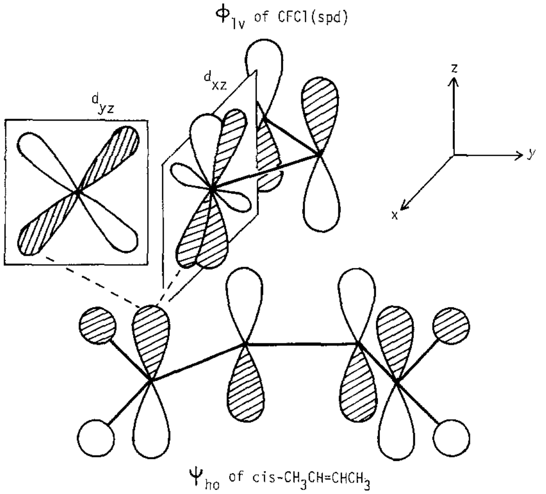

Fig. 4. Schematic representation of the ϕ_{lv} for CFCl and the ψ_{ho} for *cis*-butene-2, illustrating favorable overlappings of the Cl $d\pi$ orbitals with the CH_3 $p\pi$ orbital. The hatched lobes are minus in sign in the molecular orbitals in question. For CFCl, Eq. (13) was multiplied by -1

The functional forms of ϕ_{lv} and ψ_{ho} also match for such an interaction, as is illustrated in Fig. 4. The greater stability of the syn-Cl orientation as compared with the anti-Cl is thus ascribable to its greater $\phi_{lv} - \psi_{ho}$ interaction as a result of the spatially more favorable $p\pi - d\pi$ overlapping.

3. CH_3CCl

Moss and Mamantov [22] have recently reported that methylchlorocarbene generated by photolysis of methylchlorodiazirine adds to *cis*-butene-2 in the syn-Cl/anti-Cl ratio of 2.84. The product isomer ratio, which is relatively large, has been interpreted to be a consequence of the greater polarizability plus the lesser steric hindrance of Cl as compared with CH_3.

The interaction energies for the CH_3CCl-*cis*-butene system were calculated at $\theta = 20°$, with and without the 3*d* orbitals of Cl included. The two sets of calculations correspond to Cases 2 and 3 defined for the CFCl-*cis*-butene system. The results obtained are listed in Table 4.

A glance at the CH_3CCl data of Table 4 readily shows that, for both cases studied, the syn-Cl orientation should be significantly more stable than the anti-Cl. The large differences in E_{total} between the two orientations are ascribable to the E_Q and E_K terms, both of which greatly favor the syn-Cl orientation. This is readily understandable if one considers the electronic character and bulkiness of the methyl group relative to the chlorine atom. In both respects, the anti-Cl orientation should be disadvantageous as the methyl group of CH_3CCl lies in a closer proximity to one of the methyl groups of *cis*-butene-2.

One thing that we would like to comment on here is the relative magnitude of E_{CT} for the two orientations. When the *d* orbitals of Cl were not included, the E_{CT} was calculated to be greater in magnitude for the anti-Cl orientation. This implies that the methyl group can somehow enter into intermolecular overlap interactions at least to the same extent as the $p\pi$ orbital of the chlorine atom. By the inclusion of the Cl 3*d* orbitals into calculations, only the E_{CT} for the syn-Cl orientation is increased considerably in magnitude, just as in the case of CFCl.

Discussion

Using a ZDO version of the intermolecular-interaction theory of Murrell *et al.*, we have been able to elucidate favorable stereo courses for the addition reactions of singlet carbenes toward olefins. The syn/anti stereoselectivity of halocarbenes has been found to be influenced by various types of interaction energies altogether, no single energy term being of exclusive importance in this respect. Roughly, however, it often hinges on the balancings between charge-transfer attraction and exchange repulsion. Participation of the vacant *d* orbitals of the chlorine atom in charge transfer would also have to be stressed in this connection.

Several points might be raised, however, against the theoretical procedure adopted in this work. First, we have precluded the effect of molecular structure deformations, which should develop as the reaction proceeds. The results that the intermolecular interactions lead to net stabilization of the aggregates ($E_{\text{total}} < 0$), are at least partly ascribable to the neglect of this effect. Second, no attention has been paid to self-consistency of the molecular orbitals for components present *in* molecular aggregates. Presumably, this aspect will be of particular importance in describing intermolecular interactions associated with molecules bearing polar substituents. Third and finally, we have combined the intramolecular ZDO assumption with the intermolecular-interaction theory which was formulated in special consideration of intermolecular orbital overlaps. In a sense, the overall formalism is internally inconsistent.

Despite these inaccuracies, we believe that our present formalism is still useful as a working tool for unraveling the nature of a reaction at its early stage. The first point mentioned above is apparently beside the primary purpose of the present work. The second and third approximations would probably be tolerable in consideration of the need for a compromise between theoretical rigorousness and computational economy.

Assessments of the roles of various types of energies involved in the courses of chemical reactions are of general interest. Applications of the present method to other types of reactions (including those of carbenoids) and extensions to open-shell cases are under way and will be reported elsewhere.

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