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Reaction Paths of Some Open-Shell Reactive Intermediates

An Intermolecular Perturbation Approach

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The intermolecular interaction energy for reacting systems in singlet, triplet and doublet states was partitioned by the perturbation expansion method into the chemically meaningful five interaction terms: the Coulomb, exchange-repulsion, induction, dispersion, and charge-transfer energies. In the local ZDO approximation, these energy terms were evaluated for the dimerization of methylenes ($^{1,3}CH_2$), the additions of carbenes ($^{1,3}CH_2$ and $^{1,3}CF_2$) as well as amino radicals ($^2NH_2$ and $^2NF_2$) toward ethylene, and the hydrogen abstractions by methylenes ($^{1,3}CH_2$), nitrene (^3NH), and hydroxyl radical (^2OH) from methane. It has been found that the reaction path is much influenced by the spin-multiplicity, and that the charge-transfer and exchange-repulsion terms play a dominant role in determining the course of reactions.

Key words: Intermolecular interaction – Radicals, reaction paths of ~

1. Introduction

The chemical reactivity of carbenes and nitrenes is known to be much dependent on their spin-multiplicity. Thus, the singlet species add to the double bond of an alkene in a stereospecific way, whereas the addition of triplet species is usually nonstereospecific [1, 2]. Further, while the former species undergo insertion into a carbon-hydrogen bond of an alkane, the latter tend to favor the hydrogen abstraction [1, 2]. Theoretical investigation of such characteristic differences in reactivity caused by the difference in spin-multiplicity appears to be of general interest but has been still meager [3].

In order to understand the essential factors which govern the spin-multiplicity-specific reactions of reactive intermediates, we here wish to extend our previous intermolecular-interaction treatments [4, 5] to open-shell molecules. Our primary concern here is to analyze the reaction modes of closed-shell singlet and open-shell triplet molecules in a comparative manner, but reactions of some doublet radicals will be treated as well. The total interaction energy for given systems will be partitioned into the Coulomb, exchange-repulsion, induction, dispersion, and charge-transfer interaction terms, and their relative importances and roles will be assessed in relation with the reaction courses.

The reactions studied in this work include (1) the dimerization of methylenes ($^{1,3}CH_2$), (2) the additions of carbenes ($^{1,3}CH_2$ and $^{1,3}CF_2$) as well as amino radicals ($^2NH_2$ and $^2NF_2$) toward ethylene, and (3) the hydrogen abstractions by methylenes ($^{1,3}CH_2$), triplet nitrene (^3NH), and hydroxyl radical (^2OH) from alkanes. The results obtained seem to provide a useful insight into the modes of reaction of reactive intermediates.

2. Theoretical and Calculation Method

The theoretical method we use here is essentially that of the intermolecular configuration interaction between a closed-shell molecule and an open-shell species. Let us consider the interaction between molecule A in the closed-shell singlet state and molecule B in the doublet state. Here, we can assume without any loss of generality that molecule B has one more α-spin electron than β. The atoms in A and B are labelled by the symbols μ (with the nuclear charge Z_μ) and ν (with the nuclear charge Z_ν), respectively. The occupied and unoccupied molecular orbitals (MO) are specified with i, j, k, and l, as shown in Fig. 1. The wave functions of isolated molecules A and B may be represented by single Slater determinants built up of the orthonormal MO's:

$$\Phi_0(\mathrm{A}) = |\text{- - -} i\bar{i} \text{- - -}| \tag{1}$$

$$\Phi_0(\mathrm{B}) = |\text{- - -} j^\alpha \bar{j}^\beta \text{- - -}| \tag{2}$$

where a bar over the MO stands for the β-spin. The main feature of the present method, as compared with that of our previous work [4, 5], is that the wave function $\Phi_0(\mathrm{B})$ is constructed by the use of the unrestricted Hartree-Fock MO's [6]. Therefore, in generality, the MO j^α occupied by an α-spin electron is spatially different from the MO j^β occupied by a β-spin electron, because of the spin polarization effect.

When the two molecules come close to each other, the wave function (Ψ) of the entire interaction system can be considered to be represented as a superposition of the nonperturbed ground (AB), locally excited (A*B, and AB*), doubly excited (A*B*), and charge-transfer (A^+B^- and A^-B^+) configurations (Fig. 1):

$$\begin{aligned}
\Psi = {} & \mathcal{A}\Phi_0(\mathrm{A})\Phi_0(\mathrm{B}) + \mathcal{A}\sum_i^{\mathrm{A}}\sum_k^{\mathrm{A}} C_{i\to k}\Phi_{i\to k}(\mathrm{A}^*)\Phi_0(\mathrm{B}) \\
& + \mathcal{A}\sum_{j^\gamma}^{\mathrm{B}}\sum_{l^\gamma}^{\mathrm{B}} C_{j^\gamma\to l^\gamma}\Phi_0(\mathrm{A})\Phi_{j^\gamma\to l^\gamma}(\mathrm{B}^*) \\
& + \mathcal{A}\sum_i^{\mathrm{A}}\sum_k^{\mathrm{A}}\sum_{j^\gamma}^{\mathrm{B}}\sum_{l^\gamma}^{\mathrm{B}} C_{i\to k,\, j^\gamma\to l^\gamma}\Phi_{i\to k}(\mathrm{A}^*)\Phi_{j^\gamma\to l^\gamma}(\mathrm{B}^*) \\
& + \mathcal{A}\sum_i^{\mathrm{A}}\sum_{l^\gamma}^{\mathrm{B}} C_{i\to l^\gamma}\Phi_i(\mathrm{A}^+)\Phi_{l^\gamma}(\mathrm{B}^-) \\
& + \mathcal{A}\sum_{j^\gamma}^{\mathrm{B}}\sum_k^{\mathrm{A}} C_{j^\gamma\to k}\Phi_k(\mathrm{A}^-)\Phi_{j^\gamma}(\mathrm{B}^+)
\end{aligned} \tag{3}$$

where $\mathcal{A}$ is the antisymmetrizing operator which permits electron exchange between A and B; the symbol γ denotes the α or β-spin; and the subscripts $i \to k$ etc.

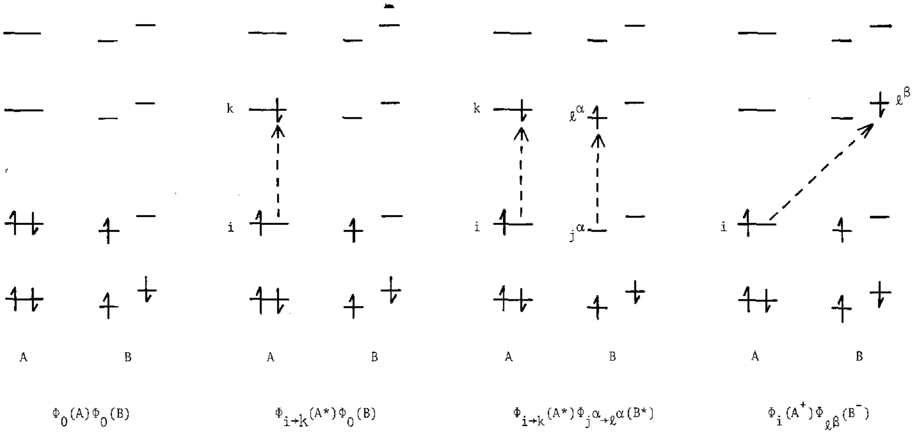

Fig. 1. Various electronic configurations which are assumed to mix as a singlet ground-state molecule A interacts with a doublet radical B.

stand for the excitation from the *i*th MO to the *k*th MO, as shown in Fig. 1. The configurations in which electrons are more heavily transferred or excited have been neglected for simplicity.

Using Eq.(3) and the perturbation expansion method similar to the one developed by Murrell *et al.* [7, 8], the total interaction energy (E_{total}) can be obtained as a sum of various terms. The energy terms of our present interest are the Coulomb (E_Q), exchange-repulsion (E_K), induction (E_I), dispersion (E_D), and charge-transfer (E_{CT}) energies, which are so termed according to the characteristics of the configurations from which they originate. To the approximation up to the second order of both the intermolecular-interaction potential and overlap, these interaction terms are expressed as follows:

$$E_Q = 2\sum_{i}^{\text{A}} \langle \rho_{ii} | V(\text{B})\rangle + \sum_{j^\alpha}^{\text{B}} \langle \rho_{j^\alpha j^\alpha} | V(\text{A})\rangle + \sum_{j^\beta}^{\text{B}} \langle \rho_{j^\beta j^\beta} | V(\text{A})\rangle$$

$$-2\sum_{i}^{\text{A}} \left\{ \sum_{j^\alpha}^{\text{B}} \langle \rho_{ii} | \rho_{j^\alpha j^\alpha}\rangle + \sum_{j^\beta}^{\text{B}} \langle \rho_{ii} | \rho_{j^\beta j^\beta}\rangle \right\} + \sum_{\mu}^{\text{A}} \sum_{\nu}^{\text{B}} z_\mu z_\nu / R_{\mu\nu} \tag{4}$$

$$E_K = -\sum_{i}^{\text{A}} \sum_{j^\alpha}^{\text{B}} \{ \langle \rho_{ij^\alpha} | \rho_{j^\alpha i}\rangle + S_{ij^\alpha}(\langle \rho_{ij^\alpha} | V(\text{B})\rangle + \rho_{j^\alpha i} | V(\text{A})\rangle)\}$$

$$-\sum_{i}^{\text{A}} \sum_{j^\beta}^{\text{B}} \{ \langle \rho_{ij^\beta} | \rho_{j^\beta i}\rangle + S_{ij^\beta}(\langle \rho_{ij^\beta} | V(\text{B})\rangle + \langle \rho_{j^\beta i} | V(\text{A})\rangle)\} \tag{5}$$

$$E_I = 2\sum_{i}^{\text{A}} \sum_{k}^{\text{A}} \langle \rho_{ik} | V(\text{B})\rangle^2 / (E_0 - E_{i\to k})$$

$$+\sum_{j^\alpha}^{\text{B}} \sum_{l^\alpha}^{\text{B}} \langle \rho_{j^\alpha l^\alpha} | V(\text{A})\rangle^2 / (E_0 - E_{j^\alpha \to l^\alpha})$$

$$+\sum_{j^\beta}^{\text{B}} \sum_{l^\beta}^{\text{B}} \langle \rho_{j^\beta l^\beta} | V(\text{A})\rangle^2 / (E_0 - E_{j^\beta \to l^\beta}) \tag{6}$$

$$E_{\mathrm{D}}=2\sum_{i}^{\mathrm{A}}\sum_{k}^{\mathrm{A}}\left\{\sum_{j^{\alpha}}^{\mathrm{B}}\sum_{l^{\alpha}}^{\mathrm{B}}\langle\rho_{ik}|\rho_{j^{\alpha}l^{\alpha}}\rangle^{2}/(E_{0}-E_{i\to k,\,j^{\alpha}\to l^{\alpha}})\right.$$
$$\left.+\sum_{j^{\beta}}^{\mathrm{B}}\sum_{l^{\beta}}^{\mathrm{B}}\langle\rho_{ik}|\rho_{j^{\beta}l^{\beta}}\rangle^{2}/(E_{0}-E_{i\to k,\,j^{\beta}\to l^{\beta}})\right\} \tag{7}$$

$$E_{\mathrm{CT}}=\sum_{i}^{\mathrm{A}}\left\{\sum_{l^{\alpha}}^{\mathrm{B}}\langle\rho_{il^{\alpha}}|V(\mathrm{B})\rangle^{2}/(E_{0}-E_{i\to l^{\alpha}})+\sum_{l^{\beta}}^{\mathrm{B}}\langle\rho_{il^{\beta}}|V(\mathrm{B})\rangle^{2}/(E_{0}-E_{i\to l^{\beta}})\right\}$$
$$+\sum_{k}^{\mathrm{A}}\left\{\sum_{j^{\alpha}}^{\mathrm{B}}\langle\rho_{j^{\alpha}k}|V(\mathrm{A})\rangle^{2}/(E_{0}-E_{j^{\alpha}\to k})+\sum_{j^{\beta}}^{\mathrm{B}}\langle\rho_{j^{\beta}k}|V(\mathrm{A})\rangle^{2}/(E_{0}-E_{j^{\beta}\to k})\right\} \tag{8}$$

where the notations and integrals used are identical with those defined in our previous paper [5], except for the interaction potential field $V(\mathrm{B})$ of molecule B in the doublet state

$$V(\mathrm{B})=\int\left\{\sum_{j^{\alpha}}^{\mathrm{B}}j^{\alpha}(2)j^{\alpha}(2)+\sum_{j^{\beta}}^{\mathrm{B}}j^{\beta}(2)j^{\beta}(2)\right\}(1/r_{12})d\tau_{2}-\sum_{\nu}^{\mathrm{B}}z_{\nu}/r_{1\nu} \tag{9}$$

and the overlap transition densities ρ_{mn} which are now written as

$$\rho_{mn}=\begin{cases}mm, & \text{when } m=n\\ mn-\sum_{p}S_{pn}mp, & \text{when } m\neq \mathrm{n}\end{cases} \tag{10}$$

The corresponding expressions for the interactions between molecules in other spin multiplicities are trivial, and hence will not be presented here.

Here, a few words on ρ_{mn} will be in order. In previous papers [4, 5], we have rather arbitrarily set $\rho_{mn}=mn-S_{mn}mm$ for $m\neq n$. This simplification resulted in the complete neglect of overlap effects upon E_{I} and E_{D}. Eq.(10) amends this defect in principle. It was ascertained, however, that the errors arising from the simplification were not so appreciable as to affect conclusions in the region of intermolecular distances treated.

In evaluating the various interaction terms numerically, we adopted similar approximations as used in previous papers [4, 5] for the sake of computational economy. Thus, the zero-differential overlaps were assumed for isolated molecules while intermolecular overlaps were retained intentionally. Mulliken's approximation was invoked for the evaluation of intermolecular multicenter atomic integrals. The wave functions and orbital energies of the isolated molecules were calculated by the CNDO/2 method [9]. The overall approximations are of course crude but do seem to be reasonable in view of the success reported earlier [4, 5]. All computations were performed on a FACOM 230-60 at the Kyoto University Computation Center.

3. Results and Discussion

3.1. *Dimerization of Methylenes* ($^{1,3}CH_2$)

It is recognized that methylene can exist both in the singlet ($^1A_1$) and triplet ($^3B_1$) states. In almost all reactions by which methylenes are generated, the

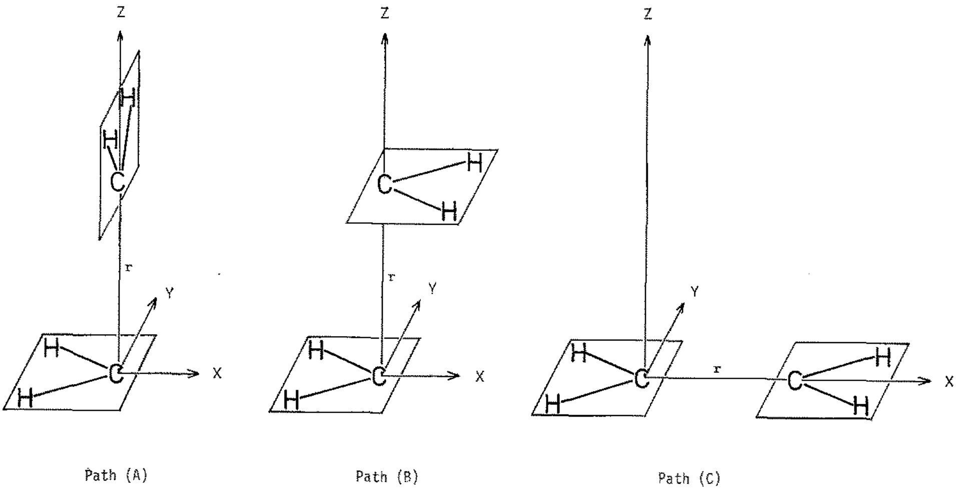

Fig. 2. Three geometries of approach assumed for the dimerization of methylenes in the singlet ($^1A_1$) and triplet ($^3B_1$) states

formally dimeric product, i.e. ethylene, is present in a sizable yield [1]. As is apparent from the orbital correlation diagrams constructed for the dimerization, the least-motion approach (with the D_{2h} symmetry) of two singlet methylenes are orbital-symmetry forbidden [10]. More favorable reaction paths for the dimerization of singlet methylenes have been investigated by molecular orbital calculations [10–13]. The one-dimensional path of reaction in the least-motion approach of two triplet methylenes, which correlates with the ground state of ethylene, has been concluded from calculations by use of the nonempirical multiconfiguration method [14].

We here consider three extreme approach models of two methylenes as shown in Fig. 2, where paths (A) and (B) are non-least-motion approaches while path (C) is the least-motion approach. In addition, we consider three spin-interaction modes (singlet-singlet, singlet-triplet and triplet-triplet) for each of the three paths. Various interaction energies calculated at a carbon-carbon distance 2.8 Å are given in Table 1.

Inspection of the data listed in Table 1 reveals the following:

(1) In the case of the singlet ($^1A_1$)-singlet ($^1A_1$) spin-interaction mode, the relative stability of the model systems decreases in the order of path (A) > path (B) > path (C). Path (C) suffers net destabilization, reflecting the fact that it is symmetry-forbidden. Clearly, the symmetry-prohibition is ascribable to the small charge-transfer stabilization (E_{CT}) and the large destabilization due to the exchange-repulsion term (E_K). The main contribution to the E_K term is the exchange repulsions between the lone pair electrons of methylenes. On the other hand, both paths (A) and (B) gain net stabilization because of the large E_{CT} stabilization far outweighing the E_K destabilization. The superiority of path (A) to path (B) is due primarily to the larger E_{CT} stabilization of the former. It was verified that the main contribution to the E_{CT} term for path (A) is the electron transfer from the

Table 1. Interaction energies in the dimerization of methylenes[a]

Spin-interaction mode	Reaction Path[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
Singlet-Singlet	(A)	−0.747	1.266	−0.044	−0.060	−5.489	−5.074
	(B)	−0.858	0.906	−0.028	−0.076	−3.316	−3.372
	(C)	−0.643	2.110	−0.018	−0.095	−0.447	0.907
Singlet-Triplet	(A)	−0.745	0.807	−0.044	−0.060	−4.204	−4.246
	(B)	−0.865	1.250	−0.067	−0.076	−4.809	−4.567
	(C)	−0.637	1.255	−0.023	−0.092	−4.137	−3.634
Triplet-Triplet	(A)	−0.731	0.895	−0.030	−0.060	−7.447	−7.373
	(B)	−0.874	1.566	−0.051	−0.078	−6.455	−5.892
	(C)	−0.602	0.411	−0.018	−0.092	−7.922	−8.223

[a] Energies given in units of kcal/mole. [b] See Fig. 2. $r = 2.8$ Å.

lone pair orbital, i.e. the highest occupied MO (HOMO), of the upper methylene to the vacant p orbital, i.e. the lowest unoccupied MO (LUMO), of the methylene in the x-y plane. Hence, the former methylene is considered to attack the latter in a nucleophilic way.

(2) In the case of the singlet ($^1A_1$)-triplet ($^3B_1$) spin-interaction mode, the relative stability increases in the order of path (C) < path (A) < path (B). For path (A), the upper methylene was assumed to be in the triplet state. Path (C) now gains net stabilization because of its relatively large E_{CT} and small E_K terms. For the three paths considered, the stabilization due to the E_{CT} term increases in the same order as for the total stability. Thus, the prevalence of path (B) over the other two is ascribable to its greatest E_{CT} stabilization. Of the various possible charge-transfer modes, the electron transfer from the half-occupied orbital of the triplet methylene to the LUMO of the singlet methylene was found to be dominant, and hence the triplet methylene is considered to act as a nucleophile.

(3) In the case of the triplet ($^3B_1$)-triplet ($^3B_1$) spin-interaction mode, which should be spin-coupled to yield an overall singlet state in an ethylenic geometry, the relative stability increases in the order of path (B) < path (A) < path (C). That is, the least-motion path (C) is the most favorable. This is ascribable to the smallest E_K term and the largest E_{CT} term in path (C). The spin-interaction mode in which two triplet methylenes are spin-coupled to give an overall quintet state (or spin-pairing of the identical spins) is expected to be energetically unfavorable. This was confirmed by calculations for path (C), which indicated that the large E_K destabilization (1.59 kcal/mole) cannot be counterbalanced by the E_{CT} stabilization (−0.88 kcal/mole).

From the results described above, we may conclude that the reaction path is much influenced by the spin-multiplicity of reactant methylenes. The spin-interaction mode (1) selects path (A) by necessity, the mode (2) tends to take path (B), and the mode (3) favors path (C). In all these cases, the charge-transfer (E_{CT}) and then exchange-repulsion (E_K) terms play a dominant role in determining the course of reaction. Other types of energies, E_Q, E_I, and E_D, are immaterial.

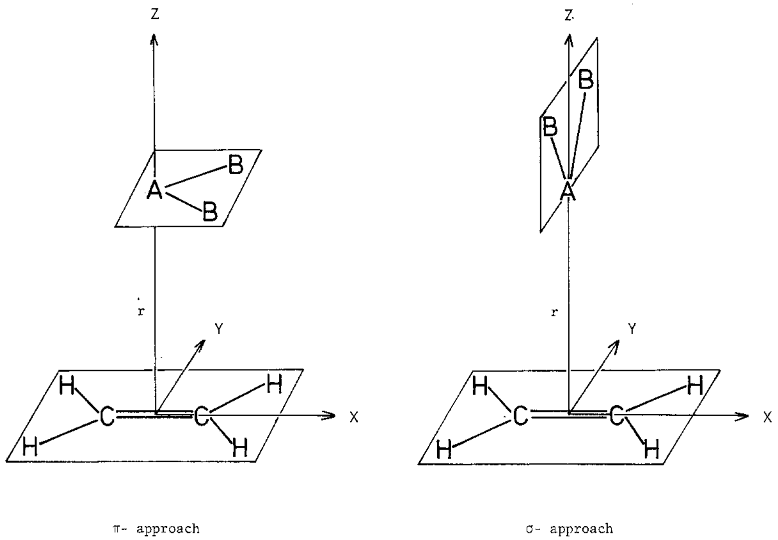

Fig. 3. The π- and σ-approaches of an AB_2-type species toward ethylene

3.2. *Additions of Carbenes ($^{1,3}CH_2$ and $^{1,3}CF_2$) and Amino Radicals ($^2NH_2$ and $^2NF_2$) toward Ethylene*

We here consider two extreme geometries of approach as shown in Fig. 3. In the π-approach the approaching AB_2 type species lies in a plane parallel to the ethylene plane, while in the σ-approach it is bound to lie in a plane perpendicular to the ethylene plane.

The addition of CH_2 to form cyclopropane has been investigated by Hoffmann using the extended Hückel method [15] and by Bodor *et al.* using the MINDO/2 method [16]. The potential surface for the addition of the singlet CF_2 has been calculated by Hoffmann *et al.* [17]. However, least attention has been paid so far to the details of the intermolecular interaction involved in the reaction.

First, we examined the addition of the $CH_2(^1A_1$ and $^3B_1)$ to ethylene. The interaction energies calculated at an intermolecular distance 3.0 Å are given in Table 2. The contributions of the interaction terms other than E_{CT} and E_K are rather small. The π-approach of the singlet CH_2 leads to net stabilization, whereas the σ-approach suffers destabilization. The superiority of the former approach to the latter owes to the much larger E_{CT} stabilization and the smaller E_K destabilization. This great contribution of the E_{CT} term is in line with the Woodward-Hoffmann selection rule for the thermal cycloaddition [18]. On the other hand, both the π- and σ-approaches of the triplet CH_2 tend to be stabilized and the σ-approach is more favorable than the π-approach, in contrast to the addition of the singlet CH_2. It was verified that all these trends remain to be true at the varying intermolecular distance r between 2.8 and 3.6 Å. The variation in reaction mode with the change in spin multiplicity would be worthy of attention.

Next, we consider the addition of $CF_2(^1A_1$ and $^3B_1)$. It is recognized that CF_2

Table 2. Interaction energies in the additions of CH_2 and CF_2 to ethylene[a]

Carbene	Spin state	Geometry of approach[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
CH_2	$^1A_1$	π	−0.517	1.303	−0.035	−0.191	−3.402	−2.842
		σ	−0.415	1.783	−0.009	−0.076	−0.330	0.953
	$^3B_1$	π	−0.498	1.824	−0.018	−0.168	−1.748	−0.608
		σ	−0.408	1.211	−0.012	−0.092	−2.311	−1.612
CF_2	$^1A_1$	π	−0.507	1.215	−0.053	−0.291	−2.375	−2.011
		σ	−0.484	1.755	−0.016	−0.104	−0.565	0.586
	$^3B_1$	π	−0.484	1.483	−0.021	−0.265	−1.584	−0.871
		σ	−0.274	1.146	−0.018	−0.120	−2.823	−2.089

[a] Energies given in units of kcal/mole. [b] See Fig. 3. $r=3.0$ Å.

has a singlet ground state [19, 20] and its reactivity to olefin is much lower than that of CH_2 [15, 21–23]. The interaction energies calculated at $r=3.0$ Å are given in Table 2. As is apparent from Table 2, the singlet CF_2 must choose the π-approach while the triplet CF_2 should favor the σ-approach, just as in the case of the addition of CH_2.

Comparisons of the results for CH_2 and CF_2 show that the singlet CH_2 should be more reactive (in π-approach) than the singlet CF_2, in agreement with observation [21–23]. The difference in reactivity seems to be ascribable to that in the magnitude of E_{CT}. Further analysis of the E_{CT} term has shown that the main contribution to E_{CT} arises from the electron transfer from the filled π-orbital (HOMO) of ethylene to the vacant p orbital (LUMO) of the carbenes. Thus, singlet carbenes are considered to act as an electrophile in their cycloaddition to olefin [24, 25]. As a corollary, $^1CH_2$ can be regarded as a stronger electrophile than CF_2.

We conclude this section by considering the addition of amino radicals to ethylene. The reactivity has received very little attention until recently. Recent work has revealed that the relatively poor reactivity of the NH_2 radical in its addition reaction to olefins is a consequence of a high energy of activation of the order of 35–40 kcal/mole [26–30]. However, the NF_2 radical is known to be considerably more reactive than NH_2 [31].

Table 3. Interaction energies in the additions of NH_2 and NF_2 to ethylene[a]

Radical	Geometry of approach[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
NH_2	π	−0.254	1.017	−0.009	−0.191	−1.130	−0.567
	σ	−0.136	0.703	−0.005	−0.076	−0.265	−0.221
NF_2	π	−0.272	0.756	−0.018	−0.288	−0.939	−0.761
	σ	−0.242	0.690	−0.007	−0.099	−0.417	−0.075

[a] Energies given in units of kcal/mole. [b] See Fig. 3. $r=3.0$ Å.

Table 4. Angular dependences of interaction energies for the CH_2–CH_4 system[a]

Spin state of CH_2	$\theta(°)$[b]	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
$^1A_1$	0	−2.073	4.031	−0.108	−0.286	−1.333	0.231
	20	−1.471	2.874	−0.155	−0.205	−2.036	−0.993
	45	−0.524	1.151	−0.058	−0.074	−2.041	−1.546
	70	−0.447	0.939	−0.035	−0.111	−2.101	−1.755
$^3B_1$	0	−2.113	2.329	−0.141	−0.304	−6.794	−7.023
	20	−1.497	1.942	−0.085	−0.210	−5.058	−4.908
	45	−0.528	1.146	−0.016	−0.071	−2.110	−1.579
	70	−0.452	1.142	−0.014	−0.108	−1.718	−1.150

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

[b] See Fig. 4. The carbon-carbon distance is fixed at 3.2 Å.

The calculation results obtained at an intermolecular distance 3.0 Å are given in Table 3. In both cases of the NH_2 and NF_2 radicals, the π-approach is advantageous over the σ-approach because of the large E_{CT} term. Interestingly enough, the desirable π-approach of NF_2 gains more net stabilization energy than does that of NH_2, despite its smaller E_{CT} stabilization. The observed greater reactivity of NF_2 as compared with NH_2 can thus be successfully accounted for. The greater stability of the NF_2 system is due primarily to its lesser E_K destabilization, a result which lends support to the qualitative view reached earlier by Shih *et al.* [26].

3.3. Hydrogen Abstractions by Methylenes ($^{1,3}CH_2$), *Nitrene* (^3NH), *and Hydroxyl Radical* (^2OH) *from Alkanes*

The coordinate system we consider for the reaction of CH_2 with methane is shown in Fig. 4, where smaller inclination angles (θ) correspond to the abstraction-like attacks while larger ones to the insertion-like attacks. The angular dependences of various interaction energies are given in Table 4.

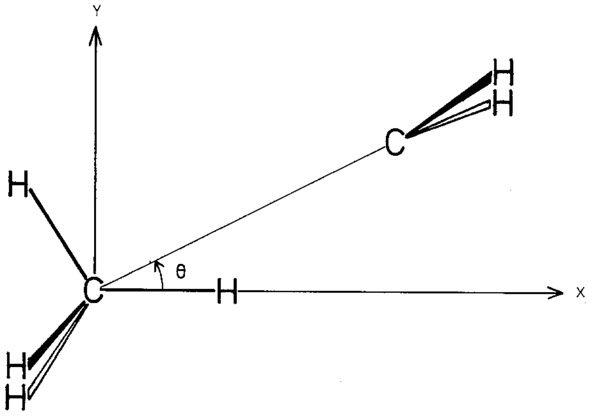

Fig. 4. Coordinate system chosen for the interaction of methylene with methane

Table 5. Partitioning of the charge transfer term for the interaction of $^3CH_2$ with CH_4[a]

Angle (θ)[b]	Electron transfer			
	from CH_4 to CH_2		from CH_2 to CH_4	
	α-spin	β-spin	α-spin	β-spin
0	−0.263	−6.047	−0.417	−0.067
20	−0.148	−4.573	−0.284	−0.051
45	−0.030	−1.976	−0.085	−0.018
70	−0.016	−1.598	−0.083	−0.018

[a] Energies given in units of kcal/mole. [b] See Fig. 4.

Table 6. Interaction energies in the hydrogen abstractions by CH_2, NH, and OH from $R^1R^2R^3CH$[a]

Substrate[b]								
R^1	R^2	R^3	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
$CH_2(^3B_1)$								
CH_3	H	H	−4.684	5.164	−0.466	−0.406	−10.579	−10.971
CH_3	CH_3	H	−4.721	5.205	−0.466	−0.452	−11.042	−11.476
CH_3	CH_3	CH_3	−4.753	5.247	−0.468	−0.491	−11.538	−12.003
$NH(^3\Sigma^-)$								
CH_3	H	H	−3.286	4.047	−0.261	−0.104	− 6.704	− 6.308
CH_3	CH_3	H	−3.312	4.091	−0.261	−0.136	− 7.110	− 6.728
CH_3	CH_3	CH_3	−3.330	4.133	−0.261	−0.141	− 7.461	− 7.060
$OH(^2\pi_i)$								
CH_3	H	H	−2.454	2.795	−0.184	−0.095	− 5.491	− 5.429
CH_3	CH_3	CH_3	−2.466	2.825	−0.187	−0.120	− 5.888	− 5.836
CH_3	CH_3	CH_3	−2.482	2.837	−0.187	−0.127	− 6.434	− 6.393

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

[b] For geometries in the case of CH_2, see Fig. 4; $\theta = 0°$, $r = 3.0$ Å. For the cases of NH and OH, the methane C–H bond and the X–H bond (X being N or O) were assumed to be collinear with the C–X distance of 3.0 Å.

As is seen in Table 4, the reaction system involving the singlet CH_2 tends to be increasingly stabilized with the increase in θ. The approach with $\theta = 0°$, in which CH_2 attacks one of the hydrogen atoms of methane along the extension of the C–H axis, suffers net destabilization. This disadvantage of the abstraction-like attack by the singlet CH_2 is ascribable to the dominantly large exchange-repulsion (E_K) term. By contrast, the triplet CH_2 can obtain a maximal stabilization at $\theta = 0°$, thus leading to the abstraction-like attack in prevalence over the insertion-like attack. The superiority of the abstraction pathway for the triplet CH_2 is caused by the small E_K destabilization outweighed by the large stabilization due primarily to the E_{CT}. It should be noted that E_{CT} is the only energy term which can by itself predict the most favorable course of reaction.

Listed in Table 5 are various composite electron-transfer energies which contribute to the E_{CT} for the reaction of the triplet CH_2. It can be seen that the main contribution to the E_{CT} term is the β-spin electron transfer from methane to CH_2. Hence, the triplet CH_2 is considered to attack methane in an electrophilic way.

Finally, we compare the hydrogen abstractions by $CH_2(^3B_1)$, $NH(^3\Sigma^-)$, and $OH(^2\pi_i)$ from various methyl-substituted methanes $R^1R^2R^3CH$, where R^1, R^2, and R^3 are either CH_3 or H. The various interaction energies calculated for these systems at $r = 3.0$ Å and $\theta = 0°$ are summarized in Table 6.

It can be seen in Table 6 that, with the triplet and doublet species here considered, the hydrogen abstraction tends to be increasingly favored in the order of primary < secondary < tertiary C–H bond. This order is in agreement with the experimental one generally concluded for the relative reactivities of the hydrogen atoms in alkanes [32, 33]. As a hydrogen atom in substrate hydrocarbons is replaced by the methyl group, both the stabilization (due to E_Q, E_D, and E_{CT}) and the destabilization (due to E_K) increase. Above all, the charge-transfer (E_{CT}) term plays a dominant role in determining the relative reactivities of various classes of hydrogen atoms. Here again, the most important contribution to the E_{CT} term is the β-spin electron transfer from the HOMO of the substrate to the LUMO of the attacking species (CH_2, NH, and OH). The abstractions should thus be electrophilic in nature.

4. Concluding Remarks

Although the applications of the present perturbation expansion method are inherently restricted to the intermolecular interactions in the region of small intermolecular overlap, it seems to provide a useful understanding of the nature of a chemical reaction at its early stage. Especially, the partitioning of the interaction energy into chemically meaningful interaction terms appears to shed insight into the factors which govern the spin-multiplicity-specific reactions of such reactive intermediates as carbenes, nitrenes, and free radicals. Because of the limited reaction model considered and the crude approximations employed in the actual calculations, we should abstain from discussing the absolute magnitude of the various interaction terms in any quantitative manner. Nevertheless, assessment of the relative importances and roles of the various interaction terms in a given reaction would still be of practical value. Within the limitation of the present approach, it may be concluded that the charge-transfer and exchange-repulsion terms play the most important role in determining the course of the reactions.

The contributions of both the charge-transfer and exchange-repulsion terms, which are in rough proportion to the intermolecular overlap, would increase progressively as the reaction proceeds to the transition state. The examination of the precise nature of the transition state is clearly beyond the scope of the present intermolecular perturbation approach. In this connection, our separate piece of work [34] based on the localized molecular orbitals points out that the reactions of open-shell molecules proceed smoothly by a general mechanism consisting of three successive stages: (1) the β-spin electron delocalization from the substrate to the attacking species, (2) the α-spin electron delocalization from the attacking species to the substrate, and (3) the concomitant local triplet excitation (spin-polarization) in the substrate. The stages (1) and (2) are responsible for the formation of new bonds as well as for the weakening of old bonds, while the stage (3) is uniquely responsible for the cleavage of the old bonds. In this sense, intermolecular perturbation approaches like the present, which consider the first stage alone, would be regarded merely as the treatments of the driving "force" for reactions. None the less, it appears that such a force can indeed be a useful probe with which we could properly infer the nature of chemical reactions.

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References

1. Kirmse,K.: Carbene chemistry, 2nd Ed. New York: Academic Press 1971
2. Lwowski,W.: Nitrenes, New York: Wiley 1970
3. Bader,R.F.W., Gangi,R.A.: J. Am. Chem. Soc. **93**, 1831 (1971)
4. Fueno,T., Nagase,S., Tatsumi,K., Yamaguchi,K.: Theoret. Chem. Acta (Berl.) **26**, 43 (1972)
5. Nagase,S., Fueno,T.: Theoret. Chim. Acta (Berl.) **35**, 217 (1974)
6. Pople,J.A., Nesbet,R.K.: J. Chem. Phys. **22**, 571 (1954)
7. Murrell,J.N., Randić,M., Williams,D.R.: Proc. Roy. Soc. (London) **A284**, 566 (1965)
8. Murrell,J.N., Shaw,G.: J. Chem. Phys. **46**, 1768 (1967)
9. Pople,J.A., Segal,G.A.: J. Chem. Phys. **44**, 3289 (1966);
   Santry,D.P., Segal,G.A.: J. Chem. Phys. **47**, 158 (1967)
10. Hoffman,R., Gleiter,R., Mallory,F.B.: J. Am. Chem. Soc. **92**, 1460 (1970)
11. Kollmar,H.: Tetrahedron Letters 3337 (1970)
12. Sustmann,R., Binsch,G.: Mol. Phys. **20**, 9 (1971)
13. Fujimoto,H., Yamabe,S., Fukui,K.: Bull. Chem. Soc. Japan **45**, 1566 (1972)
14. Basch,H.: J. Chem. Phys. **55**, 1700 (1971)
15. Hoffmann,R.: J. Am. Chem. Soc. **90**, 1475 (1968)
16. Bodor,N., Dewar,M.J.S., Wasson,J.S.: J. Am. Chem. Soc. **94**, 9095 (1972)
17. Hoffmann,R., Hayes,D.M., Skell,P.S.: J. Phys. Chem. **76**, 664 (1972)
18. Woodward,R.B., Hoffmann,R.: Angew. Chem. Intern. Ed. Engl. **8**, 781 (1969); The conservation of orbital symmetry. New York: Academic Press 1969
19. Powell,F.X., Lide,D.R.: J. Chem. Phys. **45**, 1067 (1966)
20. Mathews,C.W.: J. Chem. Phys. **45**, 1068 (1966)
21. Bethell,D.: Organic reactive intermediates, McManus,S.P., Ed. New York: Academic Press 1973
22. Mitsch,R.A., Rodgers,A.S.: Intern. J. Chem. Kinet. **1**, 439 (1969)
23. See Benson,S.W., O'Neal,H.E.: Kinetic data on gas phase unimolecular reactions, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. **21**, 248 (1970)
24. Doering,W.V.E., Henderson,W.A.: J. Am. Chem. Soc. **80**, 5274 (1958)
25. Skell,P.S., Garner,A.Y.: J. Am. Chem. Soc. **78**, 5430 (1956)
26. Shih,S., Buenker,R.J., Peyerimhoff,S.D., Michejda,C.J.: J. Am. Chem. Soc. **94**, 7620 (1972)
27. Cowley,B.R., Waters,W.A.: J. Chem. Soc. 1228 1961
28. Neale,R.S., Marcus,N.L., Schepers,R.G.: J. Am. Chem. Soc. **88**, 3051 (1966)
29. Jacobson,R.E., Johnson,K.M., Williams,G.H.: Chem. and Ind. 157 (1967)
30. Good,A., Thynne,J.C.J.: J. Chem. Soc. (B) 684 1967
31. Dijkstra,A.J., Kerr,J.A., Trotman-Dickenson,A.F.: J. Chem. Soc. (A) 105 1967
32. Ring,D.F., Rabinovitch,B.S.: Can. J. Chem. **46**, 2435 (1968)
33. Greiner,N.R.: J. Chem. Phys. **53**, 1070, 1285 (1970)
34. Nagase,S., Takatsuka,K., Fueno,T.: J. Am. Chem. Soc. (in press)

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