Morokuma, *Ibid.*, **99**, 1316 (1977); (e) K. Morokuma, *Acc. Chem. Res.*, **10**, 294 (1977).

(29) The calculated binding energy is comparable with the thermochemically estimated value (−120 kcal/mol) by U. I. Vendeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich in "Bond Energies, Ionization Potentials and Electron Affinities", translated by W. C. Price, Edward Arnold, London, 1966.

(30) In the present analyses, dispersion type interactions are not considered, though a part of electron correlation is taken into account through the UHF

formalism. For the effects of electron correlation on binding energies, see C. Hollister and O. Sinanoğlu, *J. Am. Chem. Soc.*, **88**, 13 (1966).

(31) The experimental barrier is found to be 65 kcal/mol by J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

(32) During the rotation from the planar to perpendicular form, the carbon–carbon bond distance changes from 1.36 to 1.49[7] or 1.47 Å.[6]

(33) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).

(34) L. Salem, C. Leoforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975).

An ab Initio Molecular Orbital Study of Organic Reactions. The Energy, Charge, and Spin Decomposition Analyses at the Transition State and along the Reaction Pathway

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Abstract: Ab initio molecular orbital calculations have been performed in an effort to determine what types of chemical interactions play essential roles, and how effectively the charge and spin redistributions occur at the transition state and along the reaction pathway. The reaction barrier is expressed as a sum of the intramolecular deformation energy and the intermolecular interaction energy, which in turn consists of the electrostatic, polarization, exchange repulsion, charge transfer, and their coupling terms. The importance of the intramolecular deformation is especially emphasized in relation to the efficient intermolecular interaction. The charge transfer interaction plays a much more important role in chemical reactions than in molecular complexes such as electron donor–acceptor complexes and hydrogen bonds. Furthermore, it is found that the electrostatic and polarization interactions become significant as the ionic character of the reaction is increased. The specific reaction systems we have investigated are the additions of HCl, Cl^+, CH_3^+, H^+, and H to olefins, the abstraction reactions involving CH_4 + H, CH_4 + Cl, and H_2 + $^3CH_2$, and the substitution reactions involving CH_4 + H^- and CH_3F + F^-.

I. Introduction

For a theoretical investigation of reactivities in various organic reactions, it is extremely important to elucidate what types of chemical interactions play essential roles and clarify how effectively the charge and spin redistributions occur during the course of a chemical reaction. Many earlier theoretical studies which have dealt with the problem of chemical reactivities can be divided into three groups: the static, the localization, and the delocalization approach.[2] In these approaches only a portion of chemical interactions were explicitly considered. The applications of the HOMO–LUMO interaction scheme by Fukui[3] and the symmetry rule by Woodward and Hoffmann[4] have achieved great successes in the discussion of stereochemical reactions. The successes of these methods, in principle, rely on the importance of the charge transfer interaction.[5] Some comprehensive treatments of chemical interactions have also been proposed based on the perturbation method.[6-12] However, the applications of such treatments have been limited to a rather early stage of reaction because of the inherent nature of the perturbation method. Furthermore, the effects of molecular deformations during the reaction were not considered explicitly. The molecular deformation becomes increasingly important with the progress of reaction and should have a significant influence on the reaction mechanisms.

In an effort to clarify the essential features of apparently complicated organic reactions, it seems of practical value to employ procedures which could give chemically meaningful visualization and interpretation of reactions. To this end, the reaction energy (ΔE) is expressed as a sum of the intramo-lecular deformation (DEF) energy and the intermolecular interaction (INT) energy, which in turn consists of the electrostatic (ES), polarization (PL), exchange repulsion (EX), charge transfer (CT), and their coupling (MIX) terms. Our primary interest is on the qualitative determination of the relative importance of various interactions in the transition state and the reaction intermediate.

The specific reaction systems we have investigated are the additions of HCl, Cl^+, CH_3^+, H^+, and H to olefins, the abstraction reactions of CH_4 + H, CH_4 + Cl, and H_2 + $^3CH_2$, and the substitution reactions of CH_4 + H^- and CH_3F + F^-. These systems include the cationic, anionic, neutral, radical, and triplet reactions. Our hope is that the essential features of the interaction and bond interchange in these reactions can be understood from a unified point of view.

II. Computational Details

Computation. All calculations reported here were performed within the framework of the ab initio LCAO MO SCF theory, employing a modified version of the GAUSSIAN 70 programming system.[13] The split-valence 4-31G basis sets were used with recommended exponents, contraction coefficients, and scale factors.[14] The 4-31G basis set is flexible enough to give a reasonable estimate of the interaction energy and its components.[15-17] However, it does have a tendency to exaggerate the polarity of molecules. Electron population analyses were carried out using the minimal STO-3G basis set[18] for easier visualization.

Molecular Geometries. The molecular geometries of C_2H_4 + H and C_2H_3F + H were optimized using the STO-3G basis

set. For $C_2H_4 + Cl^+$,[19] $C_2H_4 + CH_3^+$,[20] $C_2H_4 + H^+$,[21] and $C_2H_4 + HCl$,[22] the published geometries optimized using the STO-3G basis set were employed. The 4-31G optimized geometry was used for $CH_4 + H$.[23] The optimized geometries by Baybutt,[24] by Motell and Fink,[25] and by Baskin et al.[26] were used for $CH_3X + X^-$ (X = H or F), $CH_4 + Cl$, and $H_2 + {}^3CH_2$, respectively.

Interaction Energy and Deformation Energy. Our component analyses of the energy, the charge distribution, and the spin distribution were performed following several conceptual steps required in going from isolated reactant molecules to the interacting system of interest. In order to match the physical concept of chemical bond, the reaction energy (ΔE) is expressed as the sum of the intramolecular deformation (DEF) energy and the intermolecular interaction (INT)[27] energy. That is to say: (a) Initially both reactant molecules are geometrically and electronically deformed to take the value which is best suited for the interacting situation. This step gives the destabilization (DEF energy), and is similar to the "promotion" of atoms for molecule formation. (b) The deformed molecules are brought together to the intermolecular distance under consideration without changing the electron densities. In this step, the intermolecular interaction is purely electrostatic (ES). (c) The electron densities of step (b) are now brought to the best value in the interacting system by allowing various intermolecular interactions to take place such as the electron exchange (EX) between the reactants, the charge transfer (CT) from one reactant to the other and vice versa, the polarization (PL) of one reactant by the presence of the other and vice versa, and the coupling (MIX) of these effects.[28] The reaction energy (ΔE) is expressed as

$$\Delta E = DEF + INT$$

$$INT = ES + PL + EX + CT + MIX$$

The same equations can be written for the charge and spin distributions, except that ES does not change these distributions. The actual evaluations of the components in the intermolecular interaction were performed within the closed-shell or open-shell UHF single-determinant scheme according to the procedure by Morokuma and Kitaura–Morokuma.[27] Our scheme is closely related to the analysis of a chemical bond by Ruedenberg.[29] However, our analysis seems much simpler from the point of view of chemical interpretation.

III. Electrophilic Addition Reactions

For the addition of electrophiles, XY, to unsaturated bonds, two limiting reaction mechanisms have been considered.[30] One is a molecular addition which proceeds stereospecifically via a cyclic four-center transition state and exclusively occurs with cis stereochemistry. The other is a stepwise addition[31] via a carbonium ion intermediate which rapidly collapses to either a cis product or a mixture of cis and trans products depending
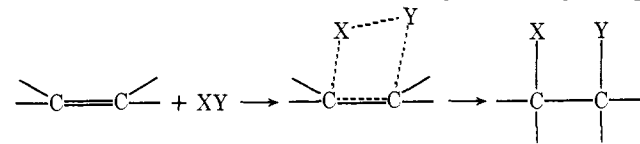
on whether the cationic intermediate has an open structure or a bridged (onium ion) structure. The addition mechanism
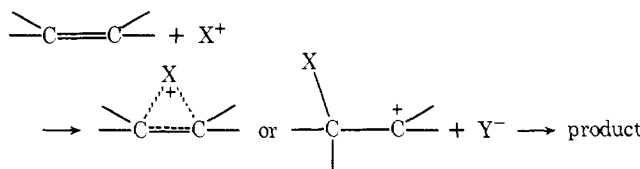
closely corresponds to the reverse of the mechanism of elimination reactions.[33]

Table I. Energy Components for the Transition State in the Addition of HCl to $CH_2=CH_2{}^a$

	With deformation	Without deformation
ES	−86.8	−59.9
EX	181.8	191.1
PL	−25.7	−21.2
CT	−76.1	−63.6
MIX	26.3	22.5
INT	19.5	68.9
DEF	28.6	0.0
ΔE	48.1	68.9

^{a} Energies are given in units of kcal/mol.

A. $H_2C=CH_2 + HCl \rightarrow H_3C-CH_2Cl$. We first consider the reaction of HCl with ethylene as an example of the molecular addition and examine the relative importance of various interactions at the transition state. The calculated energy components at the transition state are given in Table I where a negative (positive) value corresponds to stabilization (destabilization). The reaction barrier ΔE of 48 kcal/mol[34] arises from the intramolecular deformation DEF (60%) and intermolecular interaction INT (40%) energies. The DEF energy is a sum over two molecules: 9 (HCl) and 19 kcal/mol (C_2H_4). If the deformations of the reactant molecules are not permitted at all, the reaction barrier is increased to 69 kcal/mol. The INT energy is a sum of the repulsive (208 kcal/mol) and the attractive (−189 kcal/mol) energy. The attraction is 46% ES, 13% PL, and 41% CT, while the repulsion is mainly due to the EX interaction. The dominance of the repulsion over the attraction results in the ineffective intermolecular interaction.[35] However, it should be noted that the repulsive dominance is relaxed to a considerable extent by the molecular deformations. The important role of the CT as well as ES and PL interactions is evident from our energy component analyses, whereas Benson et al.[36] assumed a semi-ion pair model of the four-center cyclic transition state and calculated the activation energy by means of an electrostatic model of point dipoles. A further decomposition of the CT energy gives $CT(C_2H_4 \rightarrow HCl) = -42.4$ kcal/mol and $CT(HCl \rightarrow C_2H_4) = -30.1$ kcal/mol,[37] reflecting the electrophilic nature of the addition of HCl to C_2H_4.

Next we turn to the charge reorganization caused by the interactions at the transition state. In Tables II and III are given the component analyses for the electron population
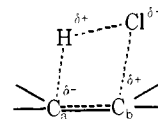
pertinent to the reaction centers. Table II shows that both old bonds C_a-C_b and H–Cl are weakened, almost exclusively by the CT interaction, augmented by DEF and PL. The CT interaction reduces the electron density in the bonding region of old bonds. For the new bonds C_a-H and C_b-Cl, the EX and CT interactions play essential roles and have the opposite effects. The former decreases the bond electron population and the latter increases it. However, the antibonding contribution of the former is overshadowed by the larger bonding contribution of the latter, resulting in net bonding. The effect is much larger in the C_a-H bond than in the C_b-Cl bond. The two new bonds are not formed simultaneously at the transition state but the formation of the C_b-Cl bond lags behind. Table III shows that a negative and a positive charge are produced on the atoms C_a and C_b, respectively, by the PL and CT interactions. In the meantime, a large charge separation occurs within the H–Cl bond, and almost half of the negative charge is produced on

Table II. Bond Electron Population of Isolated Molecules and Its Component Changes for the Transition State of C_2H_4 + HCl

	Old bonds		New bonds	
	C_a-C_b	H-Cl	C_a-H	C_b-Cl
Isolated molecule	0.599	0.257	0.0	0.0
Total change[a]	−0.124	−0.177	0.197	0.013
DEF[a]	−0.026	−0.040	0.0	0.0
EX[a]	0.035	0.041	−0.152	−0.072
PL[a]	−0.012	0.0	0.0	0.0
CT + MIX[a]	−0.121	−0.178	0.349	0.085

[a] A positive (negative) value indicates an increase (decrease) of electron population at the transition state.

Table III. Gross Atomic Electron Population of Isolated Molecules and Its Component Changes for the Transition State of C_2H_4 + HCl

	CH_2=CH_2		H-Cl	
	C_a	C_b	H	Cl
Isolated molecule	6.125	6.125	0.828	17.172
Total change[a]	0.118	−0.192	−0.057	0.335
DEF[a]	0.004	−0.012	−0.014	0.014
EX[a]	−0.017	0.016	−0.093	0.093
PL[a]	0.124	−0.060	0.044	−0.044
CT + MIX[a]	0.007	−0.136	0.006	0.272

[a] For the sign, see Table II.

the departing Cl atom with the aid of the CT interaction. This means that the transition state has a strong ionic character, not a biradical character.

B. CH_2=CH_2 + Cl^+. Next we consider the addition reactions which occur via a carbonium ion intermediate. The nature of bonding in the cyclic halogen cations has been a matter of considerable dispute since the proposal of a bridged bromonium ion by Roberts and Kimball.[38] The cyclic cations containing iodine and bromine have been characterized experimentally by Olah et al.[39] In an ab initio molecular orbital study, Hehre and Hiberty found that only the 1-haloethyl and the halogen-bridged system are stable entities, all other structures collapsing to one or both without activation energy.[19] In addition, a clear evidence for the bridged form of chloroethyl cation is given by a recent NMR spectral study.[40]

The energy components for the bridged chloroethyl cation are given in Table IV. The total interaction energy, ΔE, is negative (−138 kcal/mol) in spite of considerable contributions of the repulsive EX, MIX, and DEF interactions. The molecular deformation increases the total attraction; without the molecular deformation, $-\Delta E$ is reduced to 115 kcal/mol. The large attractive energy consists of ES (31%), PL (40%), and CT (29%). Further decomposition of the CT and PL energies gives (in kcal/mol)[37]

$$CT(C_2H_4 \rightarrow Cl^+) = -92.2, \; CT(Cl^+ \rightarrow C_2H_4) = -42.1$$

$$PL(C_2H_4) = -92.2, \; PL(Cl^+) = -73.3$$

These results demonstrate the importance of the charge transfer from the ethylene to the chlorine cation and the polarization of both reactants. Here it is interesting to compare the above results with the isoelectronic neutral analogue such as ethylene sulfide (with a normal three-member ring),[41] because the bridged cation is often represented as a strong π complex. The component analyses of the attractive interaction between the sulfur atom and the ethylene fragment gives ES (24%), PL (43%), an CT (33%). In this respect, the nature of the attractive energy in ethylene sulfide is very similar to that of the bridged chloroethyl cation. However, the ethylene sulfide has a much smaller binding energy ΔE (−44 kcal/mol) because of a larger repulsive contribution.

Table IV. Energy Component Analyses for the Bridged Carbonium Ion Intermediates in the Addition of Cl^+ or CH_3^+ toward Ethylene[a]

	CH_2=CH_2 + X	
	X = Cl^+	CH_3^+
ES	−135.3	−86.7
EX	243.0	154.6
PL	−175.9	−53.7
CT	−124.9	−91.2
MIX	32.9	−15.5
INT	−160.2	−92.5
DEF	22.0	37.3
ΔE	−138.2	−55.2

[a] Energies are given in units of kcal/mol.

Table V. Energy Component Analyses for the Radical and Cation Intermediates in the Addition toward Olefins[a]

	CH_2=CH_2 + X		CH_2=CHF + H·
	X = H·	H^+	
ES	−73.0	11.9	−75.3
EX	215.2	0.0	216.6
PL	−23.4	−117.1	−23.6
CT	−172.5	−144.2	−174.8
MIX	−30.1	45.0	−32.2
INT	−83.8	−204.4	−89.3
DEF	42.9	33.0	48.3
ΔE	−40.9	−171.4	−41.0

[a] Energies are given in units of kcal/mol.

In Table IV are also given the energy component analyses for the bridged C_2H_4 + CH_3^+ system for comparison. Although in this bridged cation the EX repulsion decreases, the attractive interaction (especially the PL term) is also decreased. As a consequence, the binding energy in the C_2H_4 + CH_3^+ system becomes smaller than that of the chloroethyl cation.

IV. Radical Addition Reactions

We consider the reaction of a hydrogen atom and ethylene as an example of radical additions, the reaction intermediate being the ethyl radical. For comparison purpose, the addition of a proton to ethylene is also discussed here. The major difference in these two additions is that in the cationic reaction both the bridged and open intermediates are equally possible with almost the same stability,[42,43] whereas in the radical reaction the pathway with C_{2v} symmetry becomes increasingly unstable with the progress of reaction.[44] Our calculation gives a large positive ΔE (95 kcal/mol) for the bridged structure of radical.

In Table V are given the energy components for the reaction intermediates of open structure in the radical and cationic additions. The radical intermediate has much smaller binding energy (ΔE) than the cationic. Note that the molecular deformation plays a more important role for the radical addition than the cationic addition in increasing the stability of the intermediate. Without deformation ΔE of the radical addition would have become positive (+10 kcal/mol), while ΔE of the cationic addition remains a large negative value (−149 kcal/mol).

The results of Table V clearly reveal the difference in the relative importance of interactions between the radical and cationic intermediates. In the radical intermediate the importance of the CT interaction is evident. In contrast, the PL as well as the CT interaction plays an important role in the cationic intermediate, as one might have expected. One may, however, be surprised to find that the ES interaction contributes to the destabilization in this cationic intermediate. This

Table VI. Energy Component Analyses for the Transition State in the Abstraction Reactions of $CH_4 + H$, $CH_4 + Cl$, and $H_2 + {}^3CH_2{}^a$

| | CH₄ + H | | | CH₄ + Cl | H₂ + ³CH₂ |
| | Axial | Substitution | | Axial | Axial |
	abstraction	D_{3h}	C_s	abstraction	abstraction
ES	−10.3	−34.8	−48.2	−62.0	−25.4
EX	65.9	87.4	138.8	164.6	72.2
PL	−5.0	−6.0	−8.7	−82.5	−10.3
CT	−62.1	−50.9	−83.8	−66.8	−40.7
MIX	13.3	11.9	28.9	44.3	12.0
INT	1.8	7.6	27.0	−2.4	7.8
DEF	22.6	46.5	49.4	40.3	9.6
ΔE	24.4	54.1	76.4	37.9	17.4

^{a} Energies are given in units of kcal/mol.

Table VII. Bond Electron Population of Isolated Molecules and Its Component Changes for the Transition State in the Axial Abstraction Reactions of $CH_4 + H$ and $H_2 + {}^3CH_2$

| | CH₄ + H | | H₂ + ³CH₂ | |
	Old bond	New bond	Old bond	New bond
Isolated molecule	0.386	0.0	0.396	0.0
Total change^a	−0.241	0.225	−0.146	0.125
DE^a	−0.075	0.0	−0.038	0.0
EX^a	0.029	−0.147	0.027	−0.119
PL^a	−0.005	0.0	−0.001	0.0
CT + MIX^a	−0.190	0.372	−0.134	0.244

^{a} For the sign, see Table II.

is due to the fact that a proton has no electron to exchange and therefore EX is zero. Here the ES energy arises from the interaction of the proton with the electron cloud and nuclei of ethylene. At the early stage of the proton addition the ES interaction plays a significant role in stabilization because of the proton–electron cloud interaction. As the reaction reaches the final stage, however, the proton–nuclear interaction becomes dominant and is responsible for the short-range repulsion.

In Table V are also given the energy components for the reaction $CH_2{=}CHF + H$ in order to examine the substituent effect on the radical intermediate. In the addition to unsymmetrically substituted olefins, radicals attack preferably to the unsubstituted end of an olefinic bond.[45] Results in Table V are for the preferred intermediate $CH_3\dot{C}HF$. The intermediate $CH_3\dot{C}HF$ is more favored than $CH_3\dot{C}H_2$ in terms of the INT energy (ES and CT). However, this trend is canceled completely by the DEF energy, resulting in the almost same energy ΔE.

V. Abstraction Reactions

In this section we examine the relative importance of various interactions in reactions involving abstraction by a doublet or triplet radical. The reaction $CH_4 + H$ was considered as an example of the former, and the reaction $H_2 + CH_2({}^3B_1)$ as an example of the latter type of abstraction.

The $CH_4 + H$ system is interesting because there is more than one saddle point on the potential energy surface, which leads to different products. The abstraction and the substitution (or exchange) are two major reactions. In the thermal region only the abstraction takes place, whereas both reactions can occur at high energies.[46] The model considered here is an axial abstraction in which the attacking hydrogen atom approaches one of the hydrogen atoms of CH_4 along the C–H axis, maintaining the C_{3v} symmetry.[23,47] For the substitution, two models were considered.[23,47] One is a Walden inversion model in which the attacking atom approaches the carbon atom from behind one of the C–H bonds with C_{3v} symmetry forming a transition state of D_{3h} (symmetry trigonal bipyramid). The other is a noninversion replacement model with the off-axis approach of the attacking atom toward a methane hydrogen maintaining the C_s symmetry.

In Table VI are given the energy components for the transition state in the axial abstraction as well as the two substitution models. The axial abstraction is more favorable both in the intermolecular INT and the intramolecular DEF energies than the substitutions. In all of the models considered, the reaction barrier, ΔE, arises almost exclusively from the DEF energy. As often pointed out in preceding sections, however, the reaction barrier is deduced to a considerable extent by molecular deformation. The destabilization due to the molecular deformation is compensated by the increased stabilization due to CT, ES, and PL interactions. The effect of the

CT interaction is most important for stabilization. In the substitution models, the attractive interaction is overshadowed by the large EX repulsion. In contrast, the axial-abstraction model has a relatively small EX repulsion, as compared with the substitution models. Thus, the transition state in the axial abstraction is sterically (EX) and electronically (CT) favorable.

Now we examine the effect of the attacking radical by replacing it with a bulkier and softer radical. In Table VI are also given the energy components for the transition state in the axial abstraction of $CH_4 + Cl$. Compared with the axial abstraction of $CH_4 + H$, the attractive PL and ES interactions are drastically increased. However, the EX repulsion also increases because of crowded electrons on Cl.

We now proceed to an analysis of the axial abstraction by the triplet methylene. As is seen in Table VI, there is a strong resemblance between the triplet and radical abstractions in the relative importance of the interactions. This means that the abstraction mechanism of triplet species is essentially the same as that of doublet species. Table VII shows the components of bond electron population associated with the reaction centers in the triplet and radical abstraction reactions. In both reactions the CT interaction is important in breaking the old bond and the attractive CT and repulsive EX interactions plays an essential role in the formation of the new bond.

Table VIII gives the components of the gross atomic spin and electron populations in the triplet abstraction. At the transition state the spin distribution can be represented schematically as H_2C^α ---- H^β–H^α, while the charge distribution is $H_2C^{\delta-}$ ---- $H^{\delta+}$–$H^{\delta-}$. The separation of α- and β-spin electrons in the substrate, upon the approach of two unpaired electrons of methylene, is mainly due to the CT interaction. On the other hand, the charge separation is due to the EX and CT interactions. The same situation was also found in the radical abstraction $CH_4 + H$.

VI. Substitution Reactions

The reactions studied here are two bimolecular nucleophilic substitution (S_N2) reactions:[48] $CH_4 + H^-$ and $CH_3F + F^-$. The energy components of the transition state are given in Table IX. The intramolecular deformation again plays a significant role at the transition state.

We first consider the reaction $CH_4 + H^-$. The importance of the ES and CT interactions is evident from Table IX. The transition state of this reaction is reached via the so-called Walden inversion process. In order to examine the effect of various nuclear displacements during the process, we consider a single molecular geometry on the intrinsic reaction pathway.[49] The molecular geometry we considered, which is in the
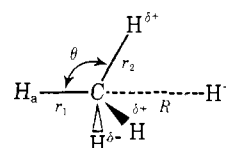
Table VIII. Gross Atomic Spin and Electron Populations of Isolated Molecules and Its Component Changes for the Transition State in the Axial Abstraction Reaction of $H_2 + {}^3CH_2{}^a$

| | Spin population[b,c] | | | Electron population[c] | | |
| | CH_2 | H–H | | CH_2 | H–H | |
	C	H_a	H_b	C	H_a	H_b
Isolated molecule	2.232	0.0	0.0	6.107	1.0	1.0
Total charge	−0.273	−0.278	0.525	0.009	−0.024	0.023
DEF	−0.024	0.0	0.0	−0.010	0.0	0.0
EX	0.002	−0.034	0.034	−0.003	−0.046	0.046
PL	−0.001	0.0	0.0	0.009	0.062	−0.062
CT + MIX	−0.250	−0.244	0.491	0.013	−0.040	0.039

^{a} For the sign, see Table II. ^{b} Spin density = (density of α electron) − (density of β electron). It is normalized to 2. ^{c} H_2C- - -H_a—H_b.

Table IX. Energy Component Analyses for the Transition State in the S_N2 Reactions of $CH_4 + H^-$ and $CH_3F + F^{-a}$

	$CH_4 + H^-$	$CH_3F + F^-$
ES	−44.8	−65.8
EX	79.1	63.6
PL	−16.3	−10.1
CT	−32.3	−30.6
MIX	−9.3	−12.7
INT	−23.6	−55.6
DEF	72.4	40.7
ΔE	48.8	−14.9

^{a} Energies are given in units of kcal/mol.

Table X. The Changes in the Energy Components by Molecular Deformations^a

| | | Partitioning to three deformation modes | | |
	Changes in energy^b	Angle θ^c	Length $r_1{}^d$	Non-additive term
ΔES	15.7	21.9	−4.2	−2.0
ΔEX	−34.1	−28.7	−4.0	−1.4
ΔPL	−3.8	−1.7	−1.8	−0.3
ΔCT	26.3	20.8	5.9	−0.4

^{a} Energies are given in units of kcal/mol. ^{b} Negative (positive) values indicate stabilization (destabilization) by molecular deformations. ^{c} Only the change in the angle θ is considered. ^{d} Only the change in the length r_1 is considered.

neighborhood of the transition state, is $r_1 = 1.33$ Å, $r_2 = 1.09$ Å, $R = 1.66$ Å, and $\theta = 93.2°$. The major nuclear displacements are the angle θ and length r_1. We calculated the change in the energy components separately for the two deformations in an effort to understand their effects. This separation is, of course, not strictly valid, as these two variables are not independent. Nonetheless, this attempt would be useful as an interpretistic tool. As is seen in Table X, the nonadditive term is rather small. This suggests that the effects of the molecular deformations could be additive in this reaction. Evidently, the effect of inversion of the nonreacting CH_3 group is dominant. The EX repulsion is reduced by the inversion, as is expected. At the same time the inversion results in the decreasing of the ES and CT stabilizations. The decreased ES term is understandable from the partially positive charge on the three hydrogen atoms in the CH_3 group. The decreasing of the CT stabilization is due to the fact that the charge transfer from the entering anion to the nonreactive CH_3 group of substrate is depressed. Interestingly the charge transfer from the entering anion to the $C-H_a$ bond to be broken is still important, as is suggested by the intermolecular configuration analysis of the wave function in terms of the localized molecular orbitals[44,50] (eq 1),

$$\Phi = 0.836\Phi_0(CH_4 \cdot H^-)$$
$$+ 0.363\Phi_{CT}(H^- \to C-H_a \text{ bond})$$
$$+ 3 \times 0.130\Phi_{CT}(H^- \to C-H \text{ bond})$$
$$+ \cdots \cdots \quad (1)$$

where the wave function Φ of the reacting system is expanded as a superposition of various electronic configurations Φ_i of reactant molecules. These results demonstrate the importance of the local property of chemical reactions.[44] In other words, the overall intermolecular interaction plays an important role in the approach of reactant molecules, but the interchange of chemical bonds is rather local in nature.

Next, we turn to the reaction $CH_3F + F^-$. As is shown in Table IX, this reaction has a much smaller (more negative) value of the energy (ΔE) than the reaction of $CH_4 + H^-$.[52] However, ES and CT interactions remain to be the most important terms. The decrease of ΔE is mainly due to an increase in the ES stabilization and a decrease in the EX and DEF destabilizations. This is understandable in terms of the strong electronegativity of the fluorine atom. The strong electronegativity of F in the substrate produces a psuedomethyl cation
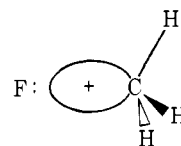
which prefers the planar structure, requiring a smaller DEF energy. The charge distribution of this deformed substrate is
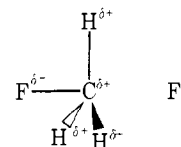
such that ES interaction with F^- is very favorable. It also makes the electron exchange between reactants ineffective, the EX interaction being decreased.

VII. Discussion and Conclusions

Behavior of the INT and DEF Energies along a Reaction Pathway. We have emphasized the important role of the intramolecular deformation at the transition state, which is often the principal source of activation energy.[53] It may be worthwhile to briefly discuss the behavior of the intramolecular DEF and intermolecular INT energies during a reaction. For this purpose, we calculated the variations in INT and DEF energies as well as in the total energy ($\Delta E = $ INT + DEF) along the reaction paths of $H_2 + {}^3CH_2{}^{26}$ and $CH_4 + H^-$.[49] The results of $H_2 + {}^3CH_2$ are shown in Figure 1. Qualitatively the same results were obtained for $CH_4 + H^-$. The trends shown in Figure 1 are believed to be common to all reactions with a reaction barrier. The DEF energy increases gradually with the progress of the reaction and begins to increase sharply as the
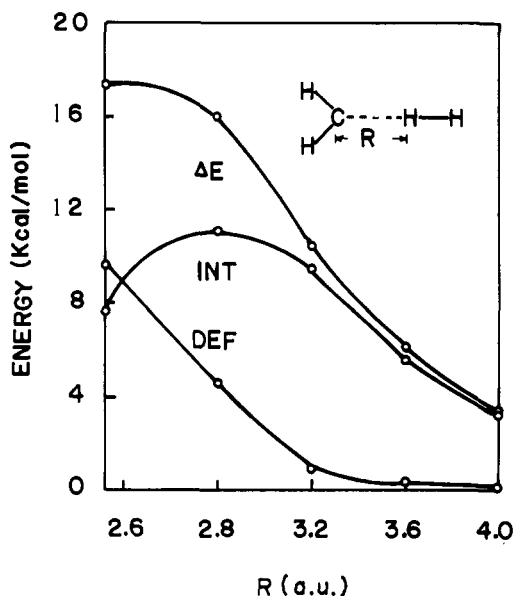
Figure 1. Variations in the intermolecular INT energy, the intramolecular DEF energy, and the reaction barrier (ΔE = INT + DEF) along the reaction pathway of $H_2 + {}^3CH_2$.

Figure 2. Variations in the energy components of the intermolecular INT energy along the reaction pathway of $H_2 + {}^3CH_2$.

Table XI. The Relative Importance of the Energy Components at the Transition State and Reaction Intermediate

	Ratio[a]	Relative importance, % ES	PL	CT
Addition Reaction				
$CH_2{=}CH_2 + CH_3{}^+$	1.60	37	23	40
$CH_2{=}CH_2 + Cl^+$	1.58	31	40	29
$CH_2{=}CH_2 + HCl$	0.91	46	13	41
$CH_2{=}CH_2 + H$	1.39	27	9	64
$CH_2{=}CHF + H$	1.41	27	9	64
Abstraction Reaction				
$CH_4 + H$	0.98	13	6	81
$CH_4 + Cl$	1.01	29	39	32
$H_2 + {}^3CH_2$	0.91	33	13	54
Substitution Reaction				
$CH_4 + H^-$	1.30	48	17	35
$CH_3F + F^-$	1.87	62	9	29

[a] The ratio of the attractive and the repulsive INT interaction.

Table XII. The Relative Importance of the Energy Components in the Hydrogen Bonded and Electron Donor-Acceptor (EDA) Complexes

	Ratio[a]	Relative importance, % ES	PL	CT
Hydrogen Bond[b]				
$H_2O{-}H_2O$	2.26	78	4	18
$H_2O{-}HF$	2.24	80	7	13
$HF{-}HF$	2.67	70	3	27
EDA Complex[c]				
$H_3N{-}BH_3$	1.48	68	12	20
$H_3N{-}ClF$	1.14	71	7	22
$OC{-}BH_3$	1.18	32	32	36

[a] The ratio of the attractive and the repulsive INT interaction. [b] Reference 16. [c] Reference 17.

reaction approaches the transition state. The INT energy increases (repulsion) at the early stage of the reaction, attains a maximum (the largest positive value), and then decreases (stabilization) significantly to reach the transition state.[54] As a consequence, the height of the reaction barrier (ΔE) at the transition state is determined from the best compromise between the increasing DEF and the decreasing INT energies. The large intramolecular deformation near the transition state is responsible for the INT stabilization. In other words, reactant molecules are significantly deformed with the aid of the effective intermolecular interactions near the transition state. The degree of the decrease in the INT energy is quite dependent on the type of chemical reaction. In some reactions the INT energy is still positive (repulsive) even at the transition state, as is shown in Figure 1. In other reactions, however, the value will be reduced to a considerable extent and will become negative (attractive). In Figure 2 are shown the variations in the energy components of the INT energy along the reaction path of $H_2 + {}^3CH_2$. The significant role of the attractive CT, ES, and PL interactions, which results in the decreasing of the INT energy near the transition state, is quite clearly shown
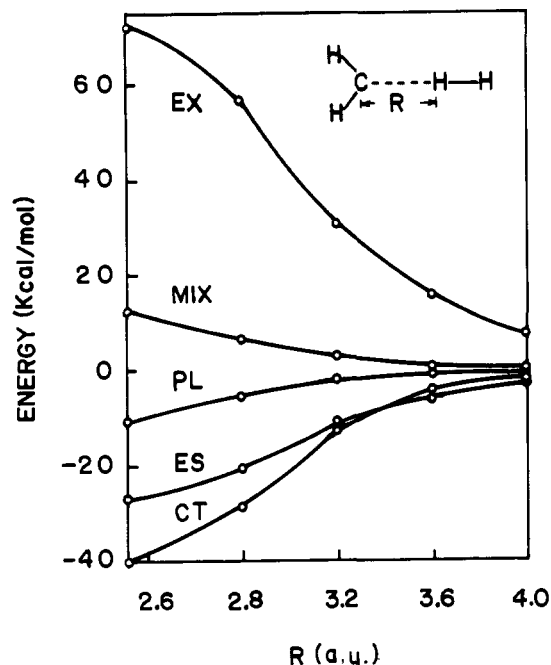
here. Essentially the same results were obtained for $CH_4 + H^-$.

It is interesting to note that at early stages of the reaction the origin of the reaction barrier arises from the INT energy. One may argue that at the incipient stage, the reactant molecules should choose a more favorable path. In fact, such a path is often available on the potential energy surface. In general, however, the reaction path causes a sudden change in the intramolecular deformation in going from reactant to the transition state. For example, in the S_N2 reaction a pathway along which the inversion of the nonreacting group is negligible or small is most favorable at the early stage of the reaction from a potential energy point of view. However, the pathway leads to the sudden umbrella opening in order to attain the transition state.[55] This means that the reaction must proceed first along an energetically less favorable pathway in order to smoothly attain the transition state. The point to be noted here is that at the early stages of the reaction, the reactant molecules cannot judge which pathway is best without trying several of them. At present, the smooth reaction pathway is determined only by calculating the reaction coordinate starting at the saddle point,[56] and is not predicted from a reactant side. Since a chemical reaction is dynamical in nature, it may be unnecessary to stick to the smooth reaction pathway.

Comparison of the Nature of Interactions among Various Reactive and Nonreactive Systems.

It is interesting to compare the nature of interactions between varieties of chemical reactions. Table XI summarizes the relative importance of three attractive energy components at the transition state or reaction intermediate. These values should also be compared with nonreactive systems, such as electron donor–acceptor (EDA) complexes and hydrogen bonded systems, shown in Table XII.

As is seen in Table XI, *the radical addition and abstraction* are dominated mainly by the CT interaction. For softer radicals the PL and ES contributions become increasingly important. In the addition of a neutral polar molecule (e.g., HCl) the ES interaction can be as important as CT. In the *cationic addition*, the PL interaction as well as CT and ES gives a significant contribution. *The nucleophilic substitution* is of ES and CT in nature, as is expected from the anionic environment. In general, the CT interaction plays an essential role in the transition state for all the reactions and the ES and PL interactions becomes significant as the ionic character of the reaction increases. The CT interaction has to take place for a bond exchange (or a chemical reaction) to occur. In addition, it is extremely important to take into account the roles of molecular deformations and the EX repulsion.

Results presented in Table XII are in sharp contrast to those of Table XI. The normal hydrogen bonds are strongly ES in nature with only a small CT contribution. The EDA complexes are a collection of complexes with different strength and origin, ranging from purely ES complexes through electrostatic supplemented by CT to ES–CT–PL complexes.[17] In no case does the CT dominate the interaction. One may conclude, therefore, that the largest single factor distinguishing reactive systems from nonreactive systems is the charge transfer interaction.

References and Notes

(1) (a) The University of Rochester; (b) The Institute for Molecular Science.
(2) For the details, see K. Fukui, "Theory of Orientation and Stereoselection", Spring-Verlag, West Berlin, 1974.
(3) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971), and the early references cited therein.
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1969.
(5) For the charge transfer theory and the maximum overlap principle, see R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956).
(6) (a) J. N. Murrell, M. Randić, and D. R. Williams, *Proc. R. Soc. London, Ser. A*, **284**, 566 (1965); (b) J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **46**, 1768 (1967).
(7) L. Salem, *Discuss. Faraday Soc.*, **30**, 150 (1966); *J. Am. Chem. Soc.*, **90**, 543, 553 (1968).
(8) R. Rein and M. Pollak, *J. Chem. Phys.*, **47**, 2039 (1967).
(9) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
(10) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968).
(11) P. D. Dacre and R. McWeeny, *Proc. R. Soc. London, Ser. A*, **317**, 435 (1970).
(12) J. O. Hirschfelder, *Chem. Phys. Lett.*, **1**, 325 (1967), and references cited therein.
(13) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program 236, Quantum Chemistry Program Exchange, Indiana University, 1974.
(14) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(15) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **95**, 7563 (1973); **97**, 966 (1975).
(16) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **99**, 1316 (1977).
(17) H. Umeyama, K. Morokuma, and S. Yamabe, *J. Am. Chem. Soc.*, **99**, 330 (1977).
(18) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(19) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 2665 (1974).
(20) L. Radom, J. A. Pople, V. Buss, and P. v. Schleyer, *J. Am. Chem. Soc.*, **94**, 311 (1972).
(21) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).
(22) P. C. Hiberty, *J. Am. Chem. Soc.*, **97**, 5975 (1975).
(23) S. Ehrenson and M. D. Newton, *Chem. Phys. Lett.*, **13**, 24 (1972).
(24) P. Baybutt, *Mol. Phys.*, **29**, 389 (1975).
(25) E. L. Motell and W. H. Fink, *J. Am. Chem. Soc.*, **98**, 7152 (1976).
(26) C. P. Baskin, C. F. Bender, C. W. Bauschlicher, Jr., and H. F. Schaefer III, *J. Am. Chem. Soc.*, **96**, 2709 (1974).
(27) (a) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); (b) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976).
(28) It should be noted that the order of the three steps in the reaction process can equally well be taken in a different way. That is, the molecular deformations are effectively caused only by the significant introduction of the intermolecular interactions such as ES, PL, EX, CT, and MIX terms.
(29) The formation of a chemical bond is analyzed in terms of the concepts of promotions, quasi-classical interaction, sharing penetration, sharing interference, and charge transfer by K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).
(30) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).
(31) The stepwise addition is further divided into Ad$_E$2 and Ad$_E$3 mechanisms, in the notation of Ingold,[32] depending on whether it is bimolecular or termolecular.
(32) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1953.
(33) A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).
(34) The observed and calculated activation energies at 298 K are 41 and 38 kcal/mol, respectively. See W. Tsang, *J. Chem. Phys.*, **41**, 2487 (1964), and ref 36a.
(35) According to the Woodward–Hoffmann rule,[4] 2s + 2s pericyclic reactions are symmetry forbidden. Recently, it was demonstrated on the basis of orbital phase continuity principle that such a transition state is allowed for concerted reactions when an additional lone-pair orbital of the halogen atom takes part in the bonding system (W. A. Goddard III, *J. Am. Chem. Soc.*, **94**, 793 (1972)). However, we think that the repulsion is still large and dominates the case. The relationship between symmetry-forbidden reactions and the nature of interactions will be discussed elsewhere.
(36) (a) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965); (b) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963); (c) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).
(37) The sum, CT(A → B) + CT(B → A), does not necessarily equal the total CT, the difference being a coupling between the two charge transfers, i.e., CT = CT(A → B) + CT(B → A) + CT$_{MIX}$. The total PL also has a mixing component and may be written in an analogous fashion as PL = PL(A) + PL(B) + PL$_{MIX}$.
(38) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).
(39) (a) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **89**, 4744 (1967), **90**, 947 (1968); (b) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968); (c) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); (d) G. A. Olah and R. D. Porter, **93**, 6877 (1971); (e) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *ibid.*, **94**, 1164 (1972).
(40) G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 3387 (1973).
(41) (a) For the suggestion of the cyclic three-membered ring as the most satisfactory representation of the bridged halocation, see ref 39b; (b) For the resemblance of the geometrical structure, see ref 19.
(42) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).
(43) B. Żurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973).
(44) (a) S. Nagase, K. Takatsuka, and T. Fueno, *J. Am. Chem. Soc.*, **98**, 3838 (1976); (b) S. Nagase and T. Fueno, *Bull. Chem. Soc. Jpn.*, **49**, 2920 (1976).
(45) (a) J. M. Tedder and J. C. Walton, *Acc. Chem. Res.*, **9**, 183 (1976); (b) The energy component analysis for the orientational effect in the radical addition to olefins will be discussed elsewhere.
(46) (a) R. Wolfgang, *Prog. React. Kinet.*, **3**, 97 (1965); (b) R. W. Walker, *J. Chem. Soc. A*, 2391 (1968); (c) M. J. Kunylo and R. B. Timmons, *J. Chem. Phys.*, **50**, 5076 (1969); (d) C. C. Chow and F. S. Rowland, *ibid.*, **50**, 2763, 5133 (1969); (e) R. E. Weston, Jr., and S. Ehrenson, *Chem. Phys. Lett.*, **9**, 351 (1971).
(47) K. Morokuma and R. E. Davis, *J. Am. Chem. Soc.*, **94**, 1060 (1972).
(48) For the recent review, see (a) D. J. McLennan, *Acc. Chem. Res.*, **9**, 281 (1976); (b) A. J. Parker, *Chem. Rev.* **69**, 1 (1969).
(49) K. Ishida, K. Morokuma, and A. Komornicki, *J. Chem. Phys.*, **66**, 2153 (1977).
(50) The configuration analyses were performed by the STO-3G basis. Transformation to localized molecular orbitals was done by the Edmiston and Ruedenberg method.[51]
(51) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).
(52) For the basis-set dependence of the barrier height in the S$_N$2 reaction, see (a) G. Berthier, D.-J. David, and A. Veillard, *Theor. Chim. Acta*, **14**, 329 (1969); (b) A. Dedieu and A. Veillard, *Chem. Phys. Lett.*, **10**, 631 (1971); *J. Am. Chem. Soc.*, **94**, 6730 (1972); (c) ref 24. The less flexible basis set tends to underestimate this reaction barrier. Regardless of the basis set, the reaction barrier of CH$_3$F + F$^-$ is much smaller than that of CH$_4$ + H$^-$. For the effect of electron correlation on the barrier height, see F. Keil and R. Ahlrichs, *J. Am. Chem. Soc.*, **98**, 4787 (1976).
(53) For the strict distinction between activation energy and barrier height of a reaction, see M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8**, 438 (1969).
(54) In reactions without a barrier, the INT energy will be negative and decrease monotonically from the early stages of the reaction.
(55) For the smooth reaction pathway, see ref 49.
(56) (a) The intrinsic reaction coordinate is defined by K. Fukui, *J. Phys. Chem.*, **74**, 4161 (1970). It is obtained by integrating the equations of motion for the classical trajectory which starts at the saddle point and proceeds "downhill" infinitely slowly; (b) see also ref 26 and C. W. Bauschlicher, Jr., H. F. Schaefer, III, and C. F. Bender, *J. Am. Chem. Soc.*, **98**, 1653 (1976).