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An Analysis of the Interaction Energy in Some S_N2 Reactions

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The interaction energy between an incoming group X^- and the substrate CRH_2Y at the geometry of the transition state (TS) for bimolecular nucleophilic substitution reactions (with X, Y, and R equal to H and F) has been subjected to decomposition according to the Morokuma scheme. The influence of the basis set and of the geometry chosen for the TS is examined. The results bring out regular trends in the different terms of the decomposition along the whole set of reactions, but they are not sufficient to give a rationale of the energetic factors involved in these reactions.

Key words: Nucleophilic substitution reactions – Interaction energy analysis.

1. Introduction

The theoretical study and interpretation of reactive molecular interactions has taken large advantage, in the last years, of the decomposition of the interaction energy ΔE into separate components.

The largest portion of available decompositions refers to chemical interactions where deformations of the internal geometries of the partners are neglected. In such a case the interaction energy depends only on the mutual distance and orientation of the two reaction partners A and B, denoted by the vector $\boldsymbol{R}$:

$$\Delta E_{AB}(\boldsymbol{R}) = E(AB, \boldsymbol{R}) - [E(A) + E(B)]. \tag{1}$$

Among the different schemes of decomposition, the most exploited one is that proposed by Morokuma [1], in the version adapted for the one-determinant SCF description of the reactive act. In such a scheme ΔE is partitioned into

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electrostatic (E_{es}), polarization (E_{pol}), exchange (E_{ex}) and charge transfer (E_{ct}) terms.

$$\Delta E = E_{es} + E_{pol} + E_{ex} + E_{ct}. \tag{2}$$

In the last term a distinction can be made [2] between a true charge transfer term which can be evaluated separately, and a remainder (E_{mix}) which collects all the coupling contributions out of the aforementioned terms.

It is not necessary to illustrate here the computational definition and the meaning of the contributions to ΔE, which are the object of a vast literature and the topic of numerous reviews (see, e.g. Refs. [3–9]). We recall that the examination of the decomposition of ΔE has been widely exploited to get a rationale of the different processes of molecular association and to set up simplified computational methods to predict the essential features of these processes (see, e.g. Refs. [10–12]).

Less material is available for reactions where deformation of the internal geometry of the reactants plays an important role. A method for the decomposition of ΔE in these cases has been developed by Umeyama et al. [13], but it requires an accurate knowledge of the reaction coordinate. A simpler approach, intuitively introduced by several researchers (see, e.g. Refs. [14–17]) and employed in Ref. [13] as a limiting approximation, consists in introducing an appropriate deformation in the internal geometry of the reactants (corresponding for example to the deformations found in the transition state or in the products) and then in placing the deformed species at the appropriate distance and orientation.

The interaction energy ΔE is thus given by two contributions, the first, ΔE_{def}, related to the geometry deformation, and the second, ΔE_{int}, related to the interactions among deformed species:

$$\Delta E = \Delta E_{def} + \Delta E_{int}. \tag{3}$$

The energy decomposition (Eq. 2) is applied only to ΔE_{int}, while ΔE_{def} may be analyzed with other methods [18].

The published results (see, e.g. Refs. [19–23]), indicate that the interaction energy decomposition gives interesting results about the relative importance of the ΔE components in a variety of chemical reactions. What is still lacking is a more detailed comparative analysis performed, for a given reaction mechanism, over a sufficiently large set of reagents bearing different substituents. Empirical analyses of this kind are the necessary support of interpretations of the reaction mechanism in terms of ΔE components and may represent the starting point for the elaboration of simpler approximate methods of evaluation.

In this spirit we present here the results of the ΔE_{int} decomposition for a few related chemical reactions. Attention is also paid to ancillary problems, namely the dependence of the analysis upon the geometry of the TS and upon the basis set.

2. Results and Discussion

The reactions we have considered are bimolecular nucleophilic S_N2 substitution reactions of the type:

$$X^- + CRH_2Y \rightarrow [XCRH_2Y]^- \rightarrow CRH_2X + Y^- \qquad (4)$$

with X, Y and R = H or F.

The S_N2 mechanism has been the object of numerous theoretical investigations [24–64] a part of which regards *ab initio* calculations on the systems of Eq. (4) [44–64]. The simpler cases of reaction (4) have been also subjected to decomposition either of ΔE or of other related quantities [19, 20, 61].

We report firstly some results obtained with the 4-31G basis set, that is the basis for which a larger amount of energy decompositions in the case of fixed internal geometry is available.

The deformation of CRH_2Y has been modelled on the geometries of the transition states (TS) obtained by Dedieu and Veillard [51]. The geometrical parameters of the deformed species, as well as the distance between X^- and the substrate, are reported in Table 1.

Table 2 gives the values of ΔE, ΔE_{def}, ΔE_{int} and the results of the decomposition of ΔE_{int} for the eight different chemical processes under consideration.

Some general trends in the different terms of the energy decomposition are evident. The differences in the E_{es} term in each couple of reactions having the same substrate are mainly due to the difference in the distances X—C, when X is equal to H or to F. Substitution of H with F as Y group produces a regular increase of the absolute value of E_{es}. It may be remarked that in the range of reagent separations considered in this paper the electrostatic term E_{es} cannot be simulated by the interaction of a negative unit point charge with the electrostatic potential V of the deformed substrate. This fact is due to the shape of V for the deformed species, which is rather flat at large distances and increases abruptly near the C atom. When X^- is placed at the position corresponding to

Table 1. Geometrical parameters of the TS adopted in the calculations displayed in Table 2

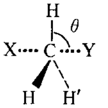
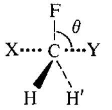
		Incoming and leaving groups
	$C-H_{eq} = 1.06$ Å $H_{eq}\hat{C}H'_{eq} = 120°$ $\theta = 90°$	$C \cdots H_{ax} = 1.737$ Å $C \cdots F_{ax} = 1.878$ Å
	$C-F_{eq} = 1.42$ Å $C-H_{eq} = 1.06$ Å $H_{eq}\hat{C}H'_{eq} = 121.07°$	$C \cdots H_{ax} = 1.601$ Å $C \cdots F_{ax} = 1.930$ Å

Table 2. Energetic values near the transition state for reactions of the type $X^- + CRH_2Y \rightarrow CRH_2X + Y^-$ (in kcal/mole)

Reactants	ΔE	ΔE_{def}	ΔE_{int}	E_{es}	E_{pol}	E_{ex}	E_{ct}
$H^- + CH_4$	48.6	72.6	−24.0	−44.8	−16.3	78.5	−41.4
$F^- + CH_4$	50.3	72.6	−22.3	−35.4	−12.2	66.9	−41.6
$H^- + CH_3F$	−17.7	44.7	−62.4	−74.4	−12.2	70.4	−46.2
$F^- + CH_3F$	−15.2	44.7	−59.9	−60.7	−10.1	50.4	−39.5
$H^- + CFH_2H$	43.6	71.7	−28.1	−78.2	−15.9	122.7	−56.7
$F^- + CFH_2H$	40.6	71.7	−31.1	−36.2	−11.2	53.6	−37.1
$H^- + CFH_2F$	−15.9	68.0	−83.9	−113.4	−13.3	114.3	−71.5
$F^- + CFH_2F$	−7.8	68.0	−75.8	−66.3	−10.4	41.1	−40.2

the TS geometry, its electronic cloud experiences a rather disymmetric potential, larger, on the average, than the potential felt by the nucleus. We report in Fig. 1 the trend of V for the four deformed species, with indication of the position of H^- and F^- in the corresponding TS geometries. Two-dimensional maps of V for a couple of these deformed molecules are reported in Ref. [65].

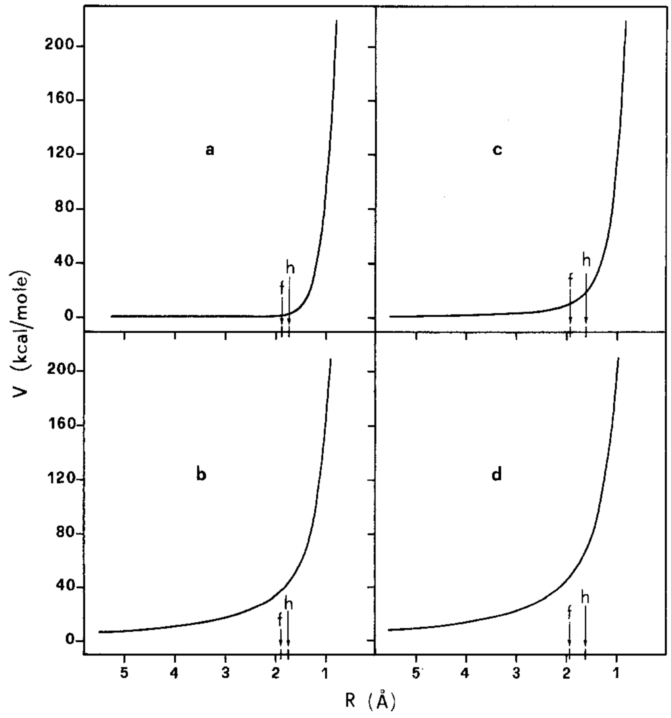


Fig. 1. Trend of the electrostatic potential of the deformed substrates CRH_2Y along the C—X axis (see the molecular schemes in Table 1): (a) CH_4, (b) CH_3F, (c) CFH_2H, (d) CFH_2F. In each diagram the position of the H^- and F^- nuclei in the geometries of the corresponding transition states is marked by the letters h and f

The polarization term is fairly constant along the whole series. It is not surprising that E_{pol} shows a lesser dependence on the distance than E_{es}, this fact having been already remarked in interaction energy dissections on undeformed molecules. On the contrary we estimate it a novel feature that, for a given X, substitution of H with F in the substrate produces a decrease of the absolute value of E_{pol}.

Regular trends are evident also in the other terms of the energy decomposition, but the examination of the data of Table 2 does not indicate a single term, or a combination of a few terms, as the leading factor in the whole set of reactions.

This negative answer is neither surprising nor discouraging. The first aim of this paper is to present a set of numerical results whose practical utility can be judged only when inserted in a larger body of similar data. The reactions chosen for this preliminary test actually present, at the same time, changes in the incoming group, in the leaving group, and in the groups directly attached to the C atom where inversion occurs. It would have been rather fortuitous if these data had given a clear-cut interpretation of the role played by the single energetic contributions in the S_N2 reactions.

There are however some related questions which deserve attention. The decompositions of ΔE for molecular interactions have shown what are the limits of singling out a specific geometry of the complex to get information on the characteristics of the process, and there is at present sufficient data to judge about the relative merits of different expansion bases of limited size. Very little is known on these questions for decompositions of ΔE with deformed geometries. The results reported in the following Tables give some information about these questions. We give, in Table 3, the decomposition of ΔE for the reaction $H^- + CH_4 \rightarrow [CH_5]^- \rightarrow CH_4 + H^-$ calculated: (A) with the STO-3G basis on a

Table 3. Comparison of the decomposition of ΔE for the reaction $H^- + CH_4 \rightarrow CH_4 + H^-$ obtained with different geometries and basis sets (in kcal/mole)

	A[a]	B[a]	C[b]	D[b]
Geometry	STO-3G	STO-3G	4-31G	4-31G
Basis	STO-3G	4-31G	STO-3G	4-31G
ΔE	46.8	59.5	60.9	48.7
ΔE_{def}	73.0	49.3	115.1	72.1
ΔE_{int}	−26.2	10.2	−54.3	−23.4
E_{es}	−34.5	−80.3	−15.0	−45.6
E_{pol}	−18.0	−15.4	−15.1	−16.3
E_{ex}	141.6	167.1	66.6	80.1
E_{ct}	−115.3	−61.2	−90.7	−41.7

[a] Geometry of the TS determined with the STO-3G basis: $r_{C-H_{ax}} = 1.481$ Å, $r_{C-H_{eq}} = 1.090$ Å, $\theta = 90°$, $H_{eq}\hat{C}H'_{eq} = 120°$.

[b] Geometry of the TS determined with the 4-31G basis: $r_{C-H_{ax}} = 1.730$ Å, $r_{C-H_{eq}} = 1.059$ Å, $\theta = 90°$, $H_{eq}\hat{C}H'_{eq} = 120°$.

geometry of the TS found with the same basis, (B) with the 4-31G basis and the same geometry as above, (C) with the STO-3G basis and the geometry of the TS obtained with the 4-31G basis, (D) with the 4-31G basis on the geometry determined with the same basis. The geometrical parameters of the two definitions of the TS are reported at the bottom of the Table. These energy decompositions can be further supplemented with the data reported in Table 2 of the present paper and in Table IX of Ref. [19] (4-31G calculations on a geometry in the neighborhood of the TS geometry).

In spite of the remarkably bad description of H^- given by the minimal basis set, calculations performed using for both basis sets the corresponding geometry (columns A and D) give comparable results for ΔE, ΔE_{def}, and ΔE_{int}. The barrier height ΔE is of course far from those given by the better SCF calculations available [50, 55–57], which range in the interval 59–70 kcal/mole. (Remark however that correlative contributions lower the barrier height of 7–15 kcal/mole [54, 55, 57]). Differences in the calculations (A) and (D) are on the contrary evident in the decomposition of ΔE_{int}. These differences are in agreement with the general trends found in the decompositions of ΔE at fixed internal geometry; the 4-31G basis predicts a larger electrostatic contribution while the STO-3G basis exaggerates the importance of the E_{ct} term.

These basis effects are more evident when one compares calculations performed with the two bases at the same geometry (columns A–B and C–D): the larger value given by the 4-31G basis for E_{ex} presumably reflects the better description of the diffuse charge distribution of the X^- fragment.

It may also be remarked that the barrier height found using the 4-31G basis on the STO-3G geometry (column B) is in fairly good agreement with the previously quoted SCF calculations of better quality. It is a common practice to use a small basis to determine the geometry and then to calculate energies with a larger basis: the good results found in the present case seem to be due to numerical chance, as the decomposition of ΔE suggests. In this case we actually have a positive value for ΔE_{int}, somewhat in contrast with intuition.

Table 4. Comparison of the decomposition of ΔE for the reaction $H^- + CH_4 \rightarrow CH_4 + H^-$ (referred to the TS geometry determined by Baybutt [56]) employing different basis sets (in kcal/mole)

Basis	A 4-31G	B Large	C Large + d	D Large + d + diff
ΔE	48.7	51.7	49.2	60.5
ΔE_{def}	72.4	71.2	71.1	70.3
ΔE_{int}	−23.6	−19.5	−21.8	−9.8
E_{es}	−44.9	−51.0	−51.4	−59.7
E_{pol}	−16.3	−15.5	−54.9	−48.7
E_{ex}	79.1	89.6	89.7	108.1
E_{ct}	−41.5	−42.6	−5.2	−9.5

[a] $r_{C-H_{ax}} = 1.735$ Å, $r_{C-H_{eq}} = 1.068$ Å, $\theta = 90°$, $H_{eq}\hat{C}H'_{eq} = 120°$.

The results of Table 3 indicate, on the whole, that decompositions of ΔE and of ΔE_{int} are sensitive to the basis and to the geometry. A complete understanding of the influence of these factors is not yet attained, but the present results indicate, in our opinion, that this goal can be reached, when applied to bases of moderate extension.

The influence of the extension of the basis set on the ΔE_{int} decomposition is considered in Table 4. We report here the results obtained at a fixed geometry for the $H^- + CH_4 \rightarrow CH_4 + H^-$ case, using: (A) the 4-31G basis, (B) a "large basis" expected to give results near the *sp* HF limit, (C) the large basis with the addition of polarization functions on C and H (respectively of *d* and *p* type), (D) the "large+polarization basis" with the addition of diffuse *s* functions on the H atoms.

These basis sets have been employed by Baybutt in an already quoted paper [56] to which reference is made for more detailed information. We have however substituted the polarization functions on C, obtained by contracting two sets of *d* orbitals, with a unique set of six *d* uncontracted functions (exponent = 0.8) which gives a better energy. The Baybutt geometry for the TS has been here adopted (see the bottom of Table 4); it may be remarked that the changes with respect to the 4-31G geometry are quite small and without significant effects on the partition of ΔE, as it may be verified by comparing column A of Table 4 with column D of Table 3.

The enlargement of the *sp* basis (column B) does not change significantly ΔE_{def} and ΔE. Among the components of ΔE_{int} the largest changes are in the E_{ex} term, partly compensated by smaller and opposite changes in E_{ex} and E_{ct}. The inclusion of polarization functions does not alter ΔE and its components ΔE_{def} and ΔE_{int}, but produces a sharp increasing of E_{pol}, compensated by an analogous decreasing in E_{ct}. The further addition of diffuse functions changes ΔE and halves ΔE_{int}, while ΔE_{def} remains practically constant. There is a further increase in E_{ex}, while E_{pol} somewhat decreases.

The enlargement of the basis set, according to the data of Table 4, may produce changes in the energy components larger than those shown by the total value ΔE. While some of these changes are reasonable as, for example, the increasing in E_{pol}, when polarization functions are added to the basis set, others have no immediate explication. This fact may be due, in part, to the intrinsic limits of the energy decomposition scheme, but it derives also, in our opinion, from artifacts due to the basis sets we have employed, which, as almost all the large bases proposed in the literature, have not been carefully optimized with respect to all the parameters relevant for molecular calculations.

Returning now to the main objective of the present note, we remark that energy decompositions are not addressed to accurate analyses of simple reactions acts, for which the very concept of decomposition is questionable [11], but, rather, to the elaboration of a rationale for whole classes of chemical interactions, for which the preliminary examination of a large body of computations, performed with a reasonable basis set, is necessary. To this end, the analyses here reported seem to indicate that the prosecution of the investigation on other S_N2 reactions performed with a basis of DZ quality may present a reasonable perspective of success.

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