$$E(d) = E_e + \tfrac{1}{2}kd^2 + k'd^3 + k''d^4 \qquad (2)$$

was used to produce a fit to the energy as a function of the displacement parameter. In eq 2 E_e represents the value of the energy at the minimum and k is equal to the harmonic force constant. The values of the asymmetric and symmetric anharmonic force constants, k' and k'' (the only two variables in eq 2), were found by minimizing the least-squares difference between the calculated energies and the corresponding values of the polynomial (**2**). The minimization procedure produced the following form of the energy as a function of the displacement parameter (energy in atomic units):

$$E(d) = (-1279.7062231) + \tfrac{1}{2}(0.0018430)d^2 + (-0.0000274)d^3 + (0.0009394)d^4 \qquad (3)$$

Next we estimated how much the anharmonic contribution in eq 3 would alter the value of the harmonic frequency. Our estimate was based on calculating the energy spectrum of the anharmonic oscillator in the potential of eq 3. Upon comparison of the harmonic and anharmonic energies for the fundamental excitation, equal to 55 and 59 cm^{-1}, respectively, we conclude that the harmonic approximation should be quite reliable in examining the S–S rocking motion.

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Supplementary Material Available: Tables of Cartesian coordinates for the optimized geometry of compounds **1**–**5** (5 pages). Ordering information is given on any current masthead page. Complete lists of the calculated vibrational modes for compounds **1**–**5** are available from the authors at the BITNET address LUDWIK@RVAX.CCIT.ARIZONA.EDU.

Charge Development at the Transition State: A Second-Order Møller–Plesset Perturbation Study of Gas-Phase S_N2 Reactions

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Abstract: A systematic analysis of the charge distribution at the transition state has been carried out for the model S_N2 reactions $N^- + CH_3X \rightarrow CH_3N + X^-$, where X = H, NH_2, OH, F, CCH, $\underline{C}N$, $\underline{N}C$, SH, and Cl for N = H and X = H, NH_2, OH, F, $\underline{C}N$, SH, and Cl for N = F. Second-order Møller–Plesset perturbation calculations indicate that for some, but not all, reactions the charges on the nucleophile and leaving group at the transition state are equal. In such cases the assumption that the transition state occurs in the vicinity of the crossing point of valence bond configurations ψ_1 and ψ_2 holds. However, in general, the contributions of the reactant and product wave functions to the transition state are not equal. With an electronegative nucleophile or leaving group, charge development on the nucleophile or leaving group at the transition state is small. A large contribution of the $N{:}^-R{:}X^-$ configuration (in addition to its contribution to the reactant and product) to the transition state leads to large charge development at the transition state. All other factors being equal, a more exothermic reaction leads to less charge development at the transition state. Also the charge distributions calculated at different theoretical levels (with and without electron correlation) are compared.

Introduction

Charge development at the transition state (TS) is central to chemistry because most reactions involve electron transfer in the transition state. An understanding of charge development at the transition state enhances our ability to predict reaction rates and to rationalize reaction mechanisms. Unfortunately, a direct study of the TS charge distribution is not a trivial problem. From a theoretical perspective it requires a proper definition of atoms in molecules, while experimentally, the charge distribution in the transition state is studied indirectly by the effects of substituents on the rate.[1]

Two completely different predictions about the TS charge distribution have appeared in the literature. The first one comes from the famous Leffler–Hammond postulate[2] which states that TS properties are related to the position of the TS along the reaction coordinate. An early TS is expected to have a reactant-like charge distribution and a later TS is predicted to have a product-like charge distribution. The other prediction comes from Shaik and Pross's valence bond configuration mixing model.[3] According to Shaik and Pross, the charge distribution at the TS is a special property and is unrelated to the position of the TS along the reaction coordinate. For simple S_N2 reactions, they predict that the charges on the entering nucleophile and leaving group are equal and that the charges do not differ from one reaction to another.[3c]

In order to understand the transition-state charge distribution and its relationship with the position of the TS along the reaction coordinate, we have carried out studies of the TS charge distribution for model S_N2 reactions. We use the charge partition method due to Bader and co-workers,[4] according to which, an atom in a molecule is defined as a real space surrounded by a zero-flux surface. The charge on an atom is obtained by subtracting the total number of electrons over the atomic basin from its nuclear

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Table I. Transition-State Integrated Charges Obtained at the HF, MP2′, and MP2 Levels (e)

	HF		MP2′		MP2	
$[N\cdots R\cdots X]^-$	$-Q_N$	$-Q_X$	$-Q_N$	$-Q_X$	$-Q_N$	$-Q_X$
$[H\cdots R\cdots NH_2]^-$	0.648	0.720	0.554	0.640	0.597	0.603
$[H\cdots R\cdots OH]^-$	0.674	0.779	0.586	0.677	0.643	0.635
$[H\cdots R\cdots F]^-$	0.711	0.832	0.629	0.717	0.700	0.679
$[H\cdots R\cdots \underline{N}C]^-$	0.750	0.792	0.657	0.724	0.698	0.705
$[H\cdots R\cdots H]^-$	0.601	0.601	0.520	0.520	0.516	0.516
$[H\cdots R\cdots CCH]^-$	0.687	0.722	0.582	0.665	0.598	0.655
$[H\cdots R\cdots \underline{C}N]^-$	0.705	0.734	0.601	0.667	0.617	0.683
$[H\cdots R\cdots SH]^-$	0.727	0.607	0.626	0.519	0.637	0.488
$[H\cdots R\cdots Cl]^-$	0.799	0.636	0.719	0.535	0.725	0.513
$[F\cdots R\cdots NH_2]^-$	0.835	0.795	0.727	0.718	0.700	0.750
$[F\cdots R\cdots OH]^-$	0.845	0.827	0.740	0.738	0.723	0.749
$[F\cdots R\cdots F]^-$	0.862	0.862	0.764	0.764	0.762	0.762
$[F\cdots R\cdots \underline{C}N]^-$	0.868	0.779	0.765	0.721	0.746	0.746
$[F\cdots R\cdots SH]^-$	0.889	0.679	0.791	0.584	0.757	0.628
$[F\cdots R\cdots Cl]^-$	0.926	0.681	0.849	0.585	0.814	0.623

charge. Our earlier studies[5] of model systems with N and X = H, OH, F, and Cl showed that the charges on the leaving group and entering nucleophile are generally not equal at the HF and MP2′ (second-order Møller–Plesset calculations carried out at the geometries optimized at the HF level) levels. However, at the MP2 level (second-order Møller–Plesset calculations with geometries optimized at the same level), cases where the leaving group and the entering nucleophile have similar charges were observed. In this contribution, a thorough study of the TS charge distribution at the MP2 level is provided and the factors which influence charge development at the TS are discussed. Also, the charge distributions calculated at different theoretical levels are compared.

Computational Methods

We have studied the model gas-phase S_N2 reactions $N^- + CH_3X \rightarrow CH_3N + X^-$, where X = H, NH_2, OH, F, CCH, $\underline{C}N$, $\underline{N}C$, SH, and Cl for N = H and X = H, NH_2, OH, F, $\underline{C}N$, SH, and Cl for N = F. (In ambiguous cases the atom which bonds to carbon is underlined.) The 6-31G basis set supplemented with diffuse and polarization functions (standard notation 6-31++G**) was used for all atoms, except the three methyl hydrogens for which the 6-31G basis set was used. The geometries were optimized at the HF and MP2(full) levels with use of the analytic gradient method. Detailed information about optimized geometries and energies can be found elsewhere.[6] The analyses were carried out at three different computational levels, namely the HF, MP2′ (second-order Møller–Plesset calculations carried out at the geometries optimized at the HF level), and MP2 (second-order Møller–Plesset calculations with geometries optimized at the same level). At the MP2′ and MP2 levels, all single and double substitutions were included in the calculations. Therefore, the energies and one-electron properties are correct to the second order.

The calculations were done by using the GAUSSIAN 80 and GAUSSIAN 86 programs and the charges were obtained by using the PROAIM and modified PROAIM packages.[7]

Results and Discussion

The HF, MP2′, and MP2 integrated charges on N and X at the TS are provided in Table I and lead to several immediate observations. First of all, at all three computational levels the charges on N and X vary substantially from one reaction to another. Second, at the HF level the charges on N and X are not equal, except in the special case of a symmetric reaction. The same observation holds at the MP2′ level. However, at the highest level, MP2, the charges on N and X are similar in some reactions and differ considerably in others. Furthermore, electron correlation effects are large. In particular, the HF method overestimates the charges on N and X at the TS. Relative to the MP2′ results, the MP2 method lowers the charge on the more electronegative group and increases the charge on the less electronegative group.[6]

According to Shaik and Pross's VBCM (valence bond configuration mixing) model,[3] there are six important VB configurations for a simple S_N2 reaction

$$\underset{\mathbf{1}}{N{:}^-\ R{\cdot\cdot}X} \qquad \underset{\mathbf{2}}{N{\cdot\cdot}R\ {:}X^-} \qquad \underset{\mathbf{3}}{N{:}^-\ R^+\ X^-} \qquad \underset{\mathbf{4}}{N{\cdot}\ R{:}^-\ {\cdot}X}$$

$$\underset{\mathbf{5}}{N{:}^-\ R{:}^-\ X^+} \qquad \underset{\mathbf{6}}{N^+\ {:}R^-\ {:}X^-}$$

The reactant wave function can be approximated by

$$\Psi_r = a_1\psi_1 + a_2\psi_3 + a_3\psi_5 \tag{1}$$

Similarly, the product wave function can be approximated by

$$\Psi_p = b_1\psi_2 + b_2\psi_3 + b_3\psi_6 \tag{2}$$

The transition-state wave function can be written as a linear combination of the VB configurations

$$\Psi_{TS} = c'_1\psi_1 + c'_2\psi_2 + c'_3\psi_3 + c'_4\psi_4 + c'_5\psi_5 + c'_6\psi_6 \tag{3}$$

Or by omitting ψ_5 and ψ_6 (which have higher energies and hence make relatively small contributions to the TS[3d,e]), the transition-state wave function can be approximated by

$$\Psi_{TS} = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 \tag{4}$$

From eq 4, it is obvious that if ψ_1 and ψ_2 make equal contributions to the TS (i.e. $c_1 = c_2$), the charges on N and X at the TS will be the same, and conversely, if N and X have equal charges at the TS, then ψ_1 and ψ_2 make equal contributions to the TS. This is because in configurations ψ_3 and ψ_4, the charges on N and X are equal. However, we must realize that in those cases where ψ_1 and ψ_2 make similar contributions to the TS, the contributions of the reactant and product wave functions to the transition state are not necessarily equal. This is illustrated by writing the TS wave function as

$$\Psi_{TS} = a\Psi_r + b\Psi_p + c\Psi_3 + d\psi_4 \tag{5}$$

Substituting for Ψ_r and Ψ_p with eqs 1 and 2, respectively, we have $c_1 = a{\cdot}a_1$ and $c_2 = b{\cdot}b_1$. Thus, it is only when $a_1 = b_1$ that equal charges on N and X ($c_1 = c_2$) indicate that the contributions of Ψ_r and Ψ_p are equal (i.e. $a = b$). The main factor which determines the contribution of ψ_1 and ψ_2 in eq 1 and 2, respectively, is the electronegativities of X and N. Highly electronegative X and N will attract more electrons to X and N in CH_3X and CH_3N. Hence, there are large contributions of ψ_3 to the reactant and product and smaller contributions of ψ_1 to the reactant and ψ_2 to the product.

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Table II. Configuration Analysis at the HF and MP2′ Levels[a]

N	X	a^2	b^2	c^2	d^2	b^2/a^2
H	NH_2	0.52	0.35	0.12	0.00	0.68
		0.55	0.42	0.03	0.00	0.76
H	OH	0.63	0.33	0.04	0.00	0.52
		0.61	0.34	0.00	0.05	0.57
H	F	0.66	0.29	0.05	0.00	0.45
		0.65	0.31	0.00	0.04	0.48
H	$\underline{N}C$	0.71	0.25	0.04	0.00	0.35
		0.68	0.28	0.00	0.04	0.42
H	H	0.40	0.40	0.20	0.00	1.00
		0.45	0.45	0.10	0.00	1.00
H	CCH	0.39	0.32	0.29	0.00	0.80
		0.47	0.39	0.14	0.00	0.83
H	$\underline{C}N$	0.44	0.30	0.27	0.00	0.68
		0.50	0.37	0.13	0.00	0.76
H	SH	0.41	0.28	0.31	0.00	0.67
		0.48	0.35	0.17	0.00	0.73
H	Cl	0.53	0.20	0.27	0.00	0.68
		0.60	0.26	0.14	0.00	0.44
F	H	0.29	0.66	0.05	0.00	2.23
		0.31	0.65	0.00	0.04	2.09
F	NH_2	0.37	0.62	0.00	0.00	1.66
		0.36	0.59	0.00	0.05	1.67
F	OH	0.45	0.53	0.00	0.02	1.19
		0.42	0.51	0.00	0.07	1.21
F	F	0.49	0.49	0.00	0.01	1.00
		0.47	0.47	0.00	0.07	1.21
F	$\underline{C}N$	0.36	0.51	0.13	0.00	1.40
		0.40	0.59	0.00	0.01	1.49
F	SH	0.32	0.43	0.25	0.00	1.32
		0.42	0.56	0.03	0.00	1.35
F	Cl	0.47	0.29	0.24	0.00	0.61
		0.54	0.40	0.06	0.00	0.75

[a] The HF results are followed by the MP2′ results.

Table III. Configuration Analysis at the MP2 Level

N	X	a^2	b^2	c^2	d^2	b^2/a^2	$\Delta E°$, kJ/mol
H	NH_2	0.60	0.38	0.02	0.00	0.63	−91.44
H	OH	0.66	0.30	0.00	0.04	0.45	−186.42
H	F	0.72	0.25	0.00	0.03	0.35	−284.86
H	$\underline{N}C$	0.71	0.24	0.00	0.05	0.34	−361.34
H	H	0.45	0.45	0.09	0.00	1.00	0.00
H	CCH	0.46	0.38	0.17	0.00	0.82	−145.90
H	$\underline{C}N$	0.47	0.36	0.17	0.00	0.76	−251.55
H	SH	0.51	0.34	0.15	0.00	0.67	−296.06
H	Cl	0.62	0.26	0.12	0.00	0.41	−399.08
F	H	0.25	0.72	0.00	0.03	2.89	284.86
F	NH_2	0.31	0.64	0.00	0.04	2.06	193.42
F	OH	0.39	0.55	0.00	0.06	1.40	98.44
F	F	0.48	0.48	0.00	0.05	1.00	0.00
F	$\underline{C}N$	0.37	0.63	0.00	0.00	1.69	33.30
F	SH	0.37	0.61	0.02	0.00	1.65	−11.20
F	Cl	0.48	0.47	0.05	0.00	0.96	−114.22

Table IV. Configuration Analysis in Terms of VB Configurations at the MP2 Level

$[N\cdots R\cdots X]^-$	c_1^2	c_2^2	c_3^2	c_4^2
$[H\cdots R\cdots NH_2]^-$	0.40	0.40	0.20	0.00
$[H\cdots R\cdots OH]^-$	0.36	0.36	0.28	0.00
$[H\cdots R\cdots F]^-$	0.32	0.30	0.38	0.00
$[H\cdots R\cdots \underline{N}C]^-$	0.29	0.30	0.40	0.00
$[H\cdots R\cdots H]^-$	0.48	0.48	0.03	0.00
$[H\cdots R\cdots CCH]^-$	0.35	0.40	0.25	0.00
$[H\cdots R\cdots \underline{C}N]^-$	0.32	0.38	0.30	0.00
$[H\cdots R\cdots SH]^-$	0.51	0.36	0.12	0.00
$[H\cdots R\cdots Cl]^-$	0.49	0.28	0.24	0.00
$[F\cdots R\cdots H]^-$	0.30	0.32	0.38	0.00
$[F\cdots R\cdots NH_2]^-$	0.25	0.30	0.45	0.00
$[F\cdots R\cdots OH]^-$	0.25	0.28	0.47	0.00
$[F\cdots R\cdots F]^-$	0.24	0.24	0.52	0.00
$[F\cdots R\cdots \underline{C}N]^-$	0.25	0.25	0.49	0.00
$[F\cdots R\cdots SH]^-$	0.37	0.24	0.38	0.00
$[F\cdots R\cdots Cl]^-$	0.38	0.19	0.44	0.00

In order to analyze the reactant and product contributions to the TS, we have recently proposed a method which uses the integrated charges in various configurations.[5,6a] Here it should be noted that Hiberty and co-workers[8] have proposed an alternative method for determining the contributions of valence bond configurations. While their method is a general method for constructing ab initio valence bond wave functions, and although it appears to be suited to the calculation of diabatic curve crossing diagrams as introduced by Shaik and Pross, a measure of the reactant and product contributions is not attempted and is not straightforward. Our method allows us to determine directly the contributions of reactant and product configurations to the wave function, which in turn can be used to study displacement of the TS parallel and perpendicular to the reaction coordinate.

The charge on atom A at the TS (Q_A) is related to the charge on atom A in the reactant ($Q_A(\Psi_r)$), in the product ($Q_A(\Psi_p)$), and in the VB configurations ψ_3 and ψ_4 ($Q_A(\psi_3)$, $Q_A(\psi_4)$) by the equation

$$Q_A = a^2Q_A(\Psi_r) + b^2Q_A(\Psi_p) + c^2Q_A(\psi_3) + d^2Q_A(\psi_4) \quad (6)$$

where $Q_A(\psi_3) = -1$ and $Q_A(\psi_4) = 0$ for A = N or X, $Q_A(\Psi_r) = -1$ for A = N, and $Q_A(\Psi_p) = -1$ for A = X.

Tables II and III list the contributions of the various configurations to the TS at the HF, MP2′, and MP2 levels,[9a] where a^2, b^2, c^2, and d^2 are the contributions from the reactant, product, and VB configurations 3 and 4, respectively, and $\Delta E°$ is the energy change of the reaction ($\Delta E° = E(CH_3N + X^-) - E(N^- + CH_3X)$). Clearly, for asymmetric reactions $a^2 \neq b^2$, i.e., the reactant contribution to the TS is not equal to that of the product. It is interesting to note that the reactions can be classified into two groups according to the ψ_3 and ψ_4 contribution to the TS, for example with N = H, the first four entries (Table III) belong to one group and the next five entries belong to the next group; similarly, when N = F, the first four and last three entries constitute distinct groups. And within each group the ratio of product to reactant contributions to the TS is related to the reaction energy. As the reaction becomes more exothermic, the ratio of product to reactant contributions to the TS decreases. This agrees with the Leffler–Hammond postulate. The more exothermic the reaction, the earlier the TS, and the more the electronic structure of the TS resembles the reactant.

Comparison of the TS electronic structures obtained at the HF, MP2′, and MP2 levels shows that the HF method overestimates the ionic character and as a result a large contribution of ψ_3 to the TS is observed. The MP2′ method gives qualitatively similar results as the MP2 method, even though the MP2′ and MP2 methods yield different charges at the TS. Thus, for properties that involve two states, the MP2′ and MP2 methods yield consistent results. This is true not only for properties that involve energies[6] but also for the one-electron properties discussed herein.

In terms of valence bond configuration contributions, the charge on A at the TS is related to the charge on A in various VB configurations by the equation

$$Q_A = c_1^2Q_A(\psi_1) + c_2^2Q_A(\psi_2) + c_3^2Q_A(\psi_3) + c_4^2Q_A(\psi_4) \quad (7)$$

A similar method[6a,9b] can be used to estimate the contributions of the various VB configurations to the TS. The results at the MP2 level are provided in Table IV. As discussed earlier, for reactions that have $Q_N \approx Q_X$, ψ_1 and ψ_2 make similar contributions to the TS, i.e. $c_1 \approx c_2$, whereas for reactions that do not have $Q_N \approx Q_X$ at the TS, ψ_1 and ψ_2 do not make similar contributions to the TS. Also the contribution of ψ_3 to the TS is significant. This is due in part to the substantial contribution of ψ_3 in the reactant

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[9] (a) The method gives the upper bound of reactant and product contributions to the TS. For further details see refs 6a and 5. (b) The method gives the upper bound of the contributions of ψ_1 and ψ_2 to the TS. For further details see ref 6a.

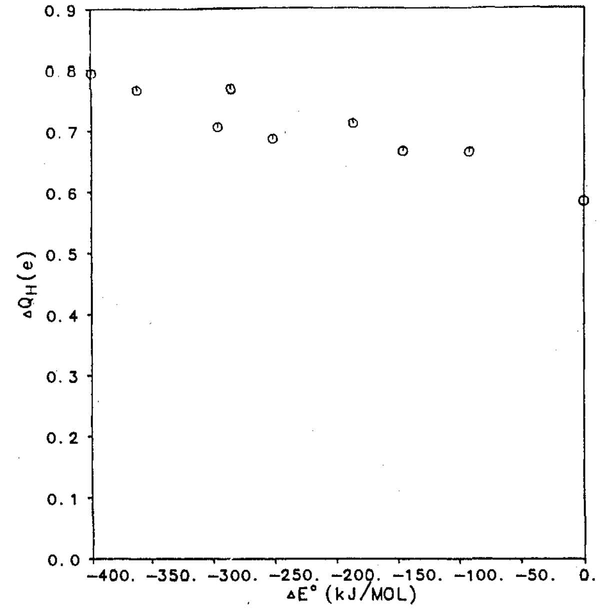

Figure 1. ΔQ_H versus ΔE° plot for $H^- + CH_3X \rightarrow CH_3H + X^-$ reactions at the MP2 level.

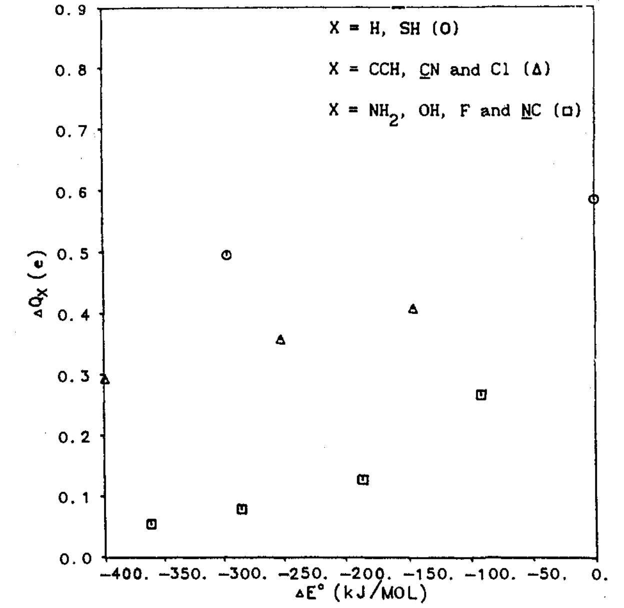

Figure 2. ΔQ_X versus ΔE° plot for $H^- + CH_3X \rightarrow CH_3H + X^-$ reactions at the MP2 level.

Table V. Integrated Charges on X in CH_3X at the HF, MP2′, and MP2 Levels (e)

	$-Q_X$		
RX	RHF	MP2′	MP2
RH	0.007	-0.066	-0.069
RNH_2	0.465	0.350	0.337
ROH	0.652	0.545	0.508
RF	0.741	0.626	0.600
R$\underline{N}$C	0.708	0.650	0.651
RCCH	0.293	0.290	0.247
R$\underline{C}$N	0.391	0.328	0.325
RSH	0.048	-0.003	-0.008
RCl	0.323	0.224	0.219

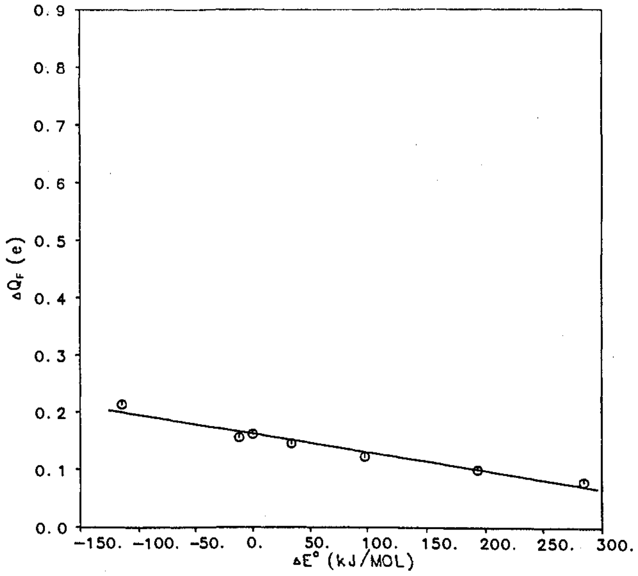

Figure 3. ΔQ_F versus ΔE° plot for $F^- + CH_3X \rightarrow CH_3F + X^-$ reactions at the MP2 level.

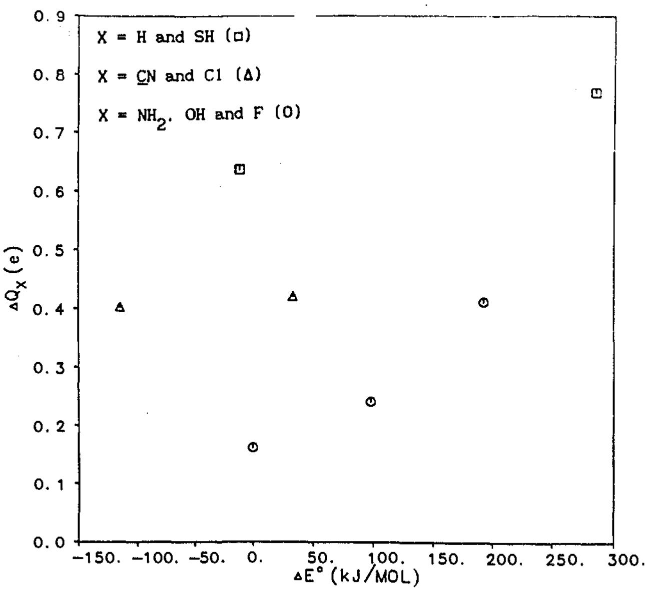

Figure 4. ΔQ_X versus ΔE° plot for $F^- + CH_3X \rightarrow CH_3F + X^-$ reactions at the MP2 level.

and product. Table V lists integrated charges on X in CH_3X molecules. Clearly, in most cases, there is a large negative charge on X, i.e. the contribution of ψ_3 is important.

Now we are in a position to discuss the factors that influence charge transfer at the TS. According to eq 6 the charge on A at the TS is determined by the charge on A in the various configurations and by the contribution of these configurations to the TS. With respect to the first factor, $Q_A(\psi_r)$ if A = X, or $Q_A(\Psi_p)$ if A = N, is related to the electronegativity of A. As noted earlier, the more electronegative A, the larger the contribution of ψ_3 in Ψ_r or Ψ_p and hence the more negative the value of $Q_A(\Psi_r)$ or $Q_A(\Psi_p)$. Whereas the charge on A in the reactant or product is affected by the electronegativity of A, $Q_A(\psi_3)$ and $Q_A(\psi_4)$ do not change as N and X vary because $Q_A(\psi_3) = -1$ and $Q_A(\psi_4) = 0$ for any N and X. With respect to the second factor, if the reactions have similar electronic structures at the TS, that is if they all have $c = 0$ or $d = 0$, the ratio of product to reactant contributions to the TS is related to the reaction energy as we discussed earlier. Thus, as the reaction becomes more exothermic, the ratio b^2/a^2 decreases and the TS charge distribution resembles the reactant more than the product. Moreover, all other things being equal, a large c^2 tends to make the charge on A at the transition state more negative.

For convenience we define the charge development on N at the transition state as

$$\Delta Q_N = |Q_N - Q_N(\Psi_p)| \qquad (8)$$

and the charge development on X as

$$\Delta Q_X = |Q_X - Q_X(\Psi_r)| \tag{9}$$

Plots of ΔQ_N and ΔQ_X as a function of reaction energy $\Delta E°$ (Figures 1–4) demonstrate clearly the factors discussed above. Figure 1 shows the charge development ΔQ_N for N = H, as a function of the reaction energy $\Delta E°$. Since N is the same for each point, the charge transfer is mainly related to the type of TS electronic structure (as determined by the values of *c* and *d*) and the reaction energy. There is a correlation, but not a very good one (compared with Figure 3), between ΔQ_N and $\Delta E°$ since these reactions do not have the same TS electronic structures. As $\Delta E°$ becomes more negative, the TS resembles the reactants more and there is a large charge transfer from the TS to the products. Figure 2 shows the charge development on leaving group X (ΔQ_X) in the same reactions. Since the electronegativities of X are not equal and the c^2 values are not the same, the charge development is not related to $\Delta E°$ in a simple fashion. Rather, the leaving groups fall within three groups according to their electronegativities and TS electronic structures. Within each group, the charge development is related to $\Delta E°$. Negative $\Delta E°$ is associated with an early TS and the transition-state structure resembles the reactants more than the products. Hence small charge development on X is observed in going from the reactant to the TS and ΔQ_X is small. Figure 3 and 4 show the corresponding plots for reactions with N = F. They exhibit the same pattern, although Figure 3 shows a better correlation than Figure 1. This is explained by the fact that for reactions with N = F, the contributions from ψ_3 and ψ_4 are all relatively small (see Table III). Thus, the reaction energy is the main factor which influences charge transfer at the TS.

From the above discussion, it is clear that charge development at the TS is not related to a single parameter. However, this does not make the charge distribution at the TS different from other properties at the TS. None of the properties at the TS is related to a single parameter. It is only within each group that a simple relationship is obtained and the effects of the other variables are virtually eliminated. Thus, for the TS charge development, we classify the reactions according to the electronic structures of the TS and the electronegativies of N and X. It is this explicit consideration of the electronegativities of N and X in the reactant and product which makes the TS charge development a property which differs from other TS properties. Those reactions which have the same TS electronic structures and similar electronegativities are said to be one group. Within each group, charge development (ΔQ_A) at the TS is related to the reaction energy ($\Delta E°$). This classification not only is useful for discussing charge development, but as we will show in a later paper this classification provides new insight into the reactions.

Conclusions

The calculations at the MP2 level indicate that for some of the reactions the charges on N and X at the TS are similar and hence for these reactions the assumption that the TS occurs in the vicinity of the crossing point of the two VB configurations ψ_1 and ψ_2 holds. However, the contributions of the reactant and product wave functions to the TS are usually not equal.

On the basis of the contributions of configurations ψ_3 and ψ_4 to the TS (see eq 5), for a given nucleophile the reactions can be classified into two groups. Thus, the MP2 data in Table III show that with H^- as the nucleophile, the first four entries belong to one group and the next five entries belong to the next group. Similarly, with F^- as the nucleophile, the first four and last three entries constitute distinct groups. Within each group, the exothermicity of the reaction increases (or equivalently the endothermicity decreases) as the ratio of product to reactant contributions to the TS (b^2/a^2 in Table III) decreases.

Charge development on the nucleophile or leaving group at the transition state is small for reactions involving an electronegative nucleophile or leaving group. This stands in sharp contrast with the large charge development at the TS which results from an increase in the contribution of VB configuration $N{:}^- \ R^+ \ {:}X^-$ to the TS wave function (*c* in eq 5 is large). Also for those reactions that have similar TS electronic structures and electronegativity factors, charge transfer at the TS is small for the more exothermic reactions.

The HF, MP2′, and MP2 integrated charges at the TS are not the same. The HF method assigns large negative charges to N and X. Relative to the HF results, the MP2 method lowers the charge on the more electronegative group (N and X) to a larger extent than on the less electronegative group. The electronic structure analysis obtained at the HF level differs qualitatively from those obtained at the MP2′ and MP2 levels. The HF method overestimates the ionic character and a contribution of ψ_3 (in eq 5) is observed in most of the reactions. The MP2′ results are consistent with those of the MP2 method. Thus, for properties that involve two electronic states, the MP2′ and MP2 methods give consistent results.

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