Theoretical Studies of Substituent Effects on S_N2 Transition States†

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Effects of substituents in the nucleophile(X), the substrate(Y) and the leaving group(Z) on the structure of S_N2 transition states have been analyzed by considering effects of four components, electrostatic(E_{es}), exchange repulsion (E_{ex}), polarization(E_{pl}) and charge transfer(E_{ct}) terms, of interaction between the reactants on the degree of bond making and bond breaking. Prediction of net effects of all substituents(X, Y and Z) on the degree of bond making were found to be clearcut whereas the effect of an electron withdrawing group on the substrate (Y = EWG) on the degree of bond breaking was complex; the substituent(Y = EWG) is normally carbon-leaving group(C*-L) bond tightening(E_{pl} dominance) but becomes C*-L bond loosening when the bond is strongly antibonding (E_{ct} dominance). Our model calculations on the reaction of CH_2XNH_2 with YCH_2COOCH_2Z using energy decomposition scheme have confirmed that predictions based on our analysis are correct.

Introduction

A numerous report has been devoted to experimental as well as theoretical works on the bimolecular nucleophilic substitution(S_N2) reaction. Recently studies of gas-phase nucleophilic displacement reactions using pulsed ion cyclotron resonance(ICR) spectroscopy[1] have provided a direct means of assessing theoretical results, albeit the reactions involved were limited to those of relatively simple ones.

Various approaches to the prediction of S_N2 transition state(TS) structure have been proposed based on rate-equilibrium relations, mostly of the qualitative nature, such as Hammond postulate[2], Bell-Evans-Polanyi principle[3], Marcus theory[4], reactivity-selectivity principle[5], and potential energy surface(PES)[6] models. Theoretically Wolfe and coworkers[7] considered variations in the S_N2 TS structure in terms of two-orbital-two-electron stabilizing(ΔE^2) and two-orbital-four-electron destabilizing(ΔE^4) interactions based on the perturbational MO(PMO) analysis, while Shaik and Pross[8] developed a model which takes into account only two major contributing(polarization and charge transfer) interactions in the TS variation. It has been shown that the models based on rate-equilibrium relations sometimes fail to predict correct variations in TS structure[8] while the quantum mechanical models(QM) seem satisfactory.[8] However the QM models also have some limitations in the prediction of the S_N2 TS structure. The PMO approach[7] can only be applied to very simple systems of tight TS structures since the two interactions considered are of the short range nature, while the quantum mechanical configuration mixing model of Shaik and Pross[8] has some ambiguities as to the effect of a leaving group on the extent of bond making and the effect of an electron withdrawing group in the substrate on the degree of bond breaking.

In this work we attempted a more general and comprehensive MO theoretical analysis of effects of substituents in the nucleophile(X), the substrate(Y) and the leaving group(Z) on transition state(TS) structure of S_N2 reactions. We will be primarily concerned with σ-donor and σ-accepter properties of the substituents and hence will be dealing only with polar effect of substituents; resonance effect on a side chain reaction center of benzene can be accounted for in a relatively simple manner so that we need not be concerned here explicitly.[9]

†Determination of Reactivity by MO Theory (Part 40).

Theory

In general there are four major components in the interaction energies ΔE of the two reacting species[10]; electrostatic(E_{es}), exchange repulsion(E_{ex}), polarization(E_{pl}) and charge transfer(E_{ct}) interactions.

$$\Delta E = E_{es} + E_{ex} + E_{pl} + E_{ct} \tag{1}$$

The electrostatic interaction(E_{es}) represents a simple coulombic attraction between a negative charge on the nucleophile and a positive charge on the substrate and hence is a stabilizing interaction. This term is first order in perturbation(V^1) and zero-th order in overlap(S^0) so that it is important at a relatively long distance between the reactants. The contribution of this interaction to the degree of bond making at the TS will therefore be substantial. Any substituent that will enhance charges on the reaction sites of the nucleophile(N) and the substrate(C*) is expected to increase magnitude of the E_{es} term. Thus an electron donating group on the nucleophile(X = EDG) and an electron withdrawing group on the substrate and on the leaving group(Y = Z = EWG) will increase the effect of this term on the bond making leading to a tighter N-C* bond.

The exchange repulsion interaction(E_{ex}) represents the closed-shell repulsion orginating from the interactions between filled orbitals of the two reactants. This term is first order in perturbation(V^1) and second order in overlap (S^2) so that it is important at a relatively short distance. We can only assess the effect of this term on the degree of bond making since the interaction is a(destabilizing) repulsive effect between the two approaching reactants. Roughly the term corresponds to the total two-orbital-four-electron interaction ΔE^4,[7]

$$\Delta E^4 = \frac{4S_{ik}(e_{ik}S_{ik} - H_{ik})}{1 - S_{ik}^2} = 4S_{ik}^2(e_{ik} - k) \tag{2}$$

where e_{ik}, S_{ik} and H_{ik} are average of two orbital energies, e_i and e_k, overlap intergral and matrix element respectively. The matrix element was approximated as $H_{ik} = kS_{ik}$, k being a negative constant. According to eq(2), consideration of the dominant frontier orbital (FMO) interaction only predicts that an electron donating substituent in the reactants(X = Y = Z = EDG) will increase the repulsion(E_{ex}) and hence decrease the N-C* bond making, since an EDG elevates the highest occupied MO(HOMO) leading to the higher level of e_{ik}.

The polarization interaction(E_{pl}) is second order in V and

zero-th order in $S(V^2S^0)$, and is also a long range term. It represents the local excitation of molecule(substrate) induced by the electrostatic field of another(nucleophile). In effect the nucleophile forces the substrate to polarize so as to reduce the electron density on nearby atoms resulting in a contraction of the exclusion shell.[11] Thus this interaction is stabilizing and the greater contribution of this term facilitates bond making. Contribution of this term(and hence bond making) will increase with the electron density of the reaction site atom(N) on the nucleophile and with the decrease in the FMO energy gap of the substrate since a greater field strength and a smaller energy gap will enhance the electron excitation within the substrate. The bond making is favored accordingly by an EDG in the nucleophile(X = EDG) and by an EWG in the substrate and the leaving group(Y = Z = EWG).[12,13] Furthermore the electron transfer leads to the electron reorganization changing the overlap populations in favor of the substrate-leaving group(C*-L) bond breaking.[11] This type of electron reorganization is facilitated by an EDG on the nucleophile(X = EDG) and by an EWG on the leaving group(Z = EWG); the C*-L bond breaking will be enhanced by these substituents. On the contrary, an EWG on the substrate(Y = EWG) will oppose such electron reorganization involved in the C*-L bond scission[8] so that the substituent (Y = EWG) will decrease bond breaking. The deformation of reactants enhance the charge transfer from the nucleophile to the substrate by modifying the shapes and levels of the MO's relevant for the interaction. Thus the polarization (E_{pl}) cooperates with the electrostatic(E_{es}) and charge transfer(E_{ct}) interactions.

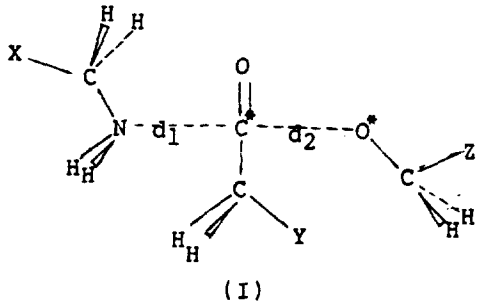
Finally the charge transfer term E_{ct} is second order in both V and $S(V^2S^2)$ and represents a short range stabilizing interaction of an electron transfer from the occupied orbital of the nucleophile to the unoccupied orbital of the substrate.[10] The predominant interaction will be an electron transfer from the HOMO of the nucleophile to the lowest unoccupied MO (LUMO) of the substrate molecule. This stabilizing interaction will be greater, the smaller the HOMO-LUMO energy gap and the greater the overlap between the two interacting orbitals. Since an electron donating group in the nucleophile (X = EDG) elevates the HOMO[12] and an electron withdrawing group in the substrate and the leaving group(Y = Z = EWG) lowers the LUMO[12], the gap will decrease and the E_{ct} term will become more stabilizing. The enhancement of this interaction will result in a greater N-C* bond making and C*-L bond breaking, since more charge is transferred from the nucleophile to the substrate(N-C*) LUMO which is antibonding for the C*-L bond. Since an EWG on the substrate (Y = EWG) decreases the FMO gap[13], both the E_{pl} and E_{ct} terms may act cooperatively to increase bond breaking for the Y = EWG, especially when the LUMO of the C*-L bond is strongly antibonding with a good leaving group.[14]

Based on our simple qualitative analysis, predictions can be made regarding effects of the four components of interaction on the degree of bond making and bond breaking as substituents X, Y and Z are varied. While the effects of substituents X and Z are clearcut and the effect of Y = EWG on the degree of N-C* bond making is clear and present no problem, the effect of Y = EWG on the degree of C*-L bond breaking is more complex since two opposing predictions are possible, *i.e.*, the E_{pl} term predicts a decrease whereas the E_{ct} term predicts an increase in bond breaking. However as we have already noted, the effect of the E_{ct} term may become dominant in favor of bond loosening for the Y = EWG when the LUMO of the C*-L bond is strongly antibonding with a good leaving group(L).[14] We have summarized the predictions regarding the degree of bond making and bond breaking in Table 1.

In this table predictions for one representative substituent each for X, Y and Z are given since effects of other substituent *i.e.*, X = EWG and Y = Z = EDG, will be the opposite to the corresponding ones listed. For the effect on bond formation the only exception is that a decrease by the E_{ex} term for X = EDG; all other terms predict an increase in bond making for X = EDG and hence the net effect will be an increase.

Calculations

In order to give a quantitative theoretical basis to our predictions in Table 1, we made a sample calculation. As a simplified model of S_N2 reaction we have chosen an attack by substituted methyl amine(NH_2CH_2X) on the carbonyl carbon of substituted methyl acetate[15](YCH_2COOCH_2Z). Since an S_N2 attack occurs at the carbonyl carbon(C*) from the rear side of the breaking bond(C*-O*)[15], the distance(d_1) between the N and C* atoms was taken as the reaction coordinate; geometries of the complex(I) with X = Y = Z = H was first optimized at an arbitrary fixed distance of $d_1 = 1.80$ A by the MNDO method.[16] The C*-O* bond length d_2 was then optimized (MNDO method) in order to assess effects of substituents (X, Y and Z) on the extent of bond breaking. The Morokuma's STO-3G energy decomposition scheme[17] was carried out on the MNDO optimized structures with various substituents to analyze effects of substituents on the various component interactions(E_{es}, E_{ex}, E_{pl} and E_{ct}) to the total interaction energies ΔE. In the analysis, optimized structure of complex(I) is divided into two fragments *i.e.*, nucleophile and substrate and interaction energy ΔE of the complex formation with $d_1 = 1.80$ A is obtained as the difference in energy between the supermolecule(I) and sum of fragments; ΔE can therefore be considered as the energy change of the N-C* bond formation in the complex(I). Hence a smaller value of ΔE should indicate a more facile bond making.



(I)

Results and Discussion

The model we adopted is of course not a TS but a reaction complex somewhere along the reaction coordinate, before and near TS. In order to confirm that the same effects are carried on to the TS we made the same calculations at a closer distance($d_1 = 1.60$ A) of approach and found that the effects on the degree of bond making and bond breaking were in fact the same in the two cases.[18]

The component interaction energies E_{es} and E_{pl} are suitable for the analysis of substituent effects in a relatively early stage of reaction as in our model calculation since they are the long range interaction terms. Again the interpretation of the E_{ex} term with our model presents no difficulty since it involves predictions on the degree of bond making only. The present model will give correct predictions as to the net effect on the bond formation in all cases; for the effect of Y = EWG on the bond breaking, the dominance of the E_{ct} term may in some cases, override the main predictions (C*–L bond tightening) based on the E_{pl} term in favor of a net C*–L bond loosening as noted above.

Effect of the Leaving Group (Substituent Effect of Z). In an S_N2 type of reaction, negative charge developes on the leaving group as the carbon–leaving group bond is broken at the TS. An electron withdrawing substituent on the leaving group(Z = EWG) will stabilize the developing negative charge and will increase the ability of the leaving group leading to a more extensive carbon–leaving group(C*–L) bond breaking as predicted in Table 1. The results of our MNDO calculations of C*–O*(d_2) distance changes as the substituent on the leaving group(Z) is varied are given in Table 2. The greater degree of bond breaking is indeed found with the more electron withdrawing substituent(Z = NO_2). Moreover reference to Table 2 indicates that the N–C* bond formation is also facilitated and hence will be greater with Z = EWG as the interaction (bond formation) energy ΔE is small; an EWG induces greater stabilization by greater electrostatic(E_{es}), polarization(E_{pl}) and charge transfer(E_{ct}) stabilization but smaller exchange repulsion(E_{ex}).

In agreement with experimental results[19] increasing the ability of the leaving group by an EWG leads to greater nucleophile–substrate bond formation and more extensive carbon–leaving group bond breaking. The same conclusion was reached by Pross and Shaik[8] applying their QM model although the effect of the leaving group change on the N–C bond formation was less clearcut with their model.

Effect of the Nucleophile (Substituent Effect of X). An electron donating group(EDG) on the nucleophile is expected to increase the nucleophile strength by increasing electronic charge on the reaction site, N atom. The increase in the nucleophile strength in turn will facilitate bond formation; a greater bond formation will then lead to greater bond cleavage since more charge will flow into the sigma antibonding LUMO of the cleaving bond.[20] The effects of substituent(X) in the nucleophile on the bond–formation and –breaking are summarized in Table 3. It can be seen from this Table that both the bond–making and –breaking are facilitated by the more electron donating substituent in agreement with the predictions in Table 1; the interaction energy(bond formation energy) ΔE is less and the bond cleavage (d_2) is greater with the more electron donating substituent, e.g., X = CH_3. In this case all the component interaction energies for X = EDG are in favor of both bond making and breaking.

The results of our calculation are in good agreement with the experimental results obtained for the benzyl system[19] and also with the prediction made by the QM model of Pross and Shaik.[8]

Effect of the Substrate (Substituent Effect of Y). Experimentally it is well known that an electron withdrawing group on the substrate(Y = EWG) normally leads to tightening of the TS[21], *i.e.*, an EWG will result in a greater N–C* bond–making and less carbon–leaving group(C*–L) bond–breaking. The effects of the substituent Y on the bond–making(ΔE) and bond–breaking(d_2) as the substituent X and Z are varied are summarized in Table 4. Inspection of the table reveals that in all cases an EWG(Y = Cl) leads to less bond breaking(smaller d_2 value) and greater bond formation (smaller ΔE value). As predicted in Table 1, the component interaction energies are in favor of more facile bond formation for the Y = EWG *i.e.*, greater stabilizing interactions of E_{es}, E_{pl} and E_{ct} and less destabilization of E_{ex}. Furthermore this table demonstrates that the conclusions reached as to the effects of substituent X and Z are true whether Y is an EWG(Y = Cl) or an EDG(Y = CH_3 or NH_2); for Z = EWG and X = EDG both the bond–breaking and –making are facilitated (*i.e.*, greater d_2 and smaller ΔE) irrespective of whether the Y is electron withdrawing(Y = Cl) or electron–donating(Y = CH_3, NH_2).

Recently we have studied the leaving group effect on the TS structure of the nucleophilic substitution reaction of benzylbenzenesulfonates with anilines in MeOH–MeCN mixtures[22] and found that a more electron withdrawing substituent on the substrate e.g. Y = p–NO_2 actually led to more extensive bond breaking instead of a decrease in the bond breaking as one would normally predict from Table 1. Since the benzenesulfonate group is a good leaving group with a strongly antibonding LUMO for the C*–L bond[14], we think that this is the case of the E_{ct} term dominance overriding the

Table 1. Theoretical Predictions of the Effects of Substituents on the Degree of Bond Formation(BF) and Bond Breaking(BB) Based on the four Component Interaction Terms

	E_{es}	E_{ex}	E_{pl}	E_{ct}	Net effect	
X = EDG	BF↑	BF↓	BF↑	BF↑	BF↑	
			BB↑	BB↑	BB↑	
Y = EWG	BF↑	BF↑	BF↑	BF↑	BF↑	
			BB↓	BB↑	BB↓	(↑)
Z = EWG	BF↑	BF↑	BF↑	BF↑	BF↑	
			BB↑	BB↑	BB↑	

Arrows "↑" and "↓" denote "increase" and "decrease" respectively.

Table 2. MNDO Results of Carbon–Leaving Group(C*–L*) Distance and Energy Decomposition of Interaction Energy ΔE(a.u.); for X = Y = H and d_1 = 1.8 A

Z	d_2(A)	E_{es}	E_{ex}	E_{pl}	E_{ct}	ΔE
CH_3	1.5023	−0.0801	0.1903	−0.0023	−0.0251	0.1101
H	1.5001	−0.0803	0.1903	−0.0022	−0.0250	0.1100
Cl	1.5230	−0.0827	0.1851	−0.0026	−0.0261	0.1024
NO_2	1.5366	−0.0834	0.1846	−0.0026	−0.0262	0.1013

Table 3. MNDO Results of Carbon–Leaving Group(C*–O*) Distance and Energy Decomposition of Interaction Energy ΔE(a.u.); for X = Z = H and d_1 = 1.8 A

X	d_2(A)	E_{es}	E_{ex}	E_{pl}	E_{ct}	ΔE
CH_3	1.5022	−0.0803	0.1902	−0.0023	−0.0250	0.1100
H	1.5001	−0.0803	0.1903	−0.0022	−0.0250	0.1100
Cl	1.4946	−0.0792	0.1932	−0.0018	−0.0249	0.1139
NO_2	1.4904	−0.0789	0.1942	−0.0018	−0.0240	0.1153

Table 4. MNDO Results of Carbon-Leaving Group(C*-O*) Distance d_2 and Energy Decomposition of Interaction Energy ΔE(a.u.); for d_1 = 1.8 A and 1.6 A (in parenthesis)

X	Y	Z	d_2(A)	E_{es}	E_{ex}	E_{pl}	E_{ct}	ΔE
H	CH_3	CH_3	1.5273	−0.0808	0.2451	−0.0023	−0.0257	0.1058
			(1.7037)	(−0.1336)	(0.3562)	(−0.0032)	(−0.0366)	(0.0988)
H	CH_3	Cl	1.5501	−0.0835	0.2435	−0.0026	−0.0266	0.0977
H	Cl	CH_3	1.5074	−0.0828	0.2437	−0.0028	−0.0271	0.0970
			(1.6355)	(−0.1348)	(0.3569)	(−0.0036)	(−0.0372)	(0.0947)
H	Cl	Cl	1.5318	−0.0853	0.2420	−0.0031	−0.0278	0.0893
			(1.7347)	(−0.1385)	(0.3519)	(−0.0048)	(−0.0394)	(0.0747)
CH_3	NH_2	H	1.5488	−0.0812	0.2436	−0.0024	−0.0261	0.1025
Cl	NH_2	H	1.5412	−0.0797	0.2414	−0.0020	−0.0255	0.1076
			(1.7878)	(−0.1272)	(0.3530)	(−0.0033)	(−0.0391)	(0.1070)
CH_3	Cl	H	1.5070	−0.0829	0.2437	−0.0028	−0.0271	0.0967)
Cl	Cl	H	1.5025	−0.0805	0.2417	−0.0023	−0.0265	0.1029
			(1.6229)	(−0.1309)	(0.3540)	(−0.0033)	(−0.0368)	(0.1052)

opposite effect(tighter C*-L bond) of the E_{pl} term on the direction of change in the bond breaking.

Finally we may encounter third kind of behavior in the degree of bond breaking for the Y = EWG, in which the effects of two opposing terms, E_{pl} and E_{ct}, may cancel out so that the bond breaking may become insensitive to the substituent Y. Experimentally this type of behavior was found in the alkaline hydrolysis of substituted phenyl benzoate.[23]

Conclusion

(i) The four component interaction energies in general predict the same changes(net effect) in the bond-making and -breaking for the substituents in the nucleophile(X), the substrate(Y) and the leaving group(Z), excepting two cases: (1) for an X = EDG the E_{ex} predicts a decrease while all other components(and hence net effect) predict an increase in bond making, and (2) for an Y = EWG bond breaking is predicted to increase by the E_{ct} term while it is predicted to decrease by the E_{pl} term.

(ii) Our model calculations on the interaction energies involved in the S_N2 reaction confirm that the predictions are all correct; the X = EDG actually had an effect of facile bond making as the net effect predicted. It was also found that the net effect of the Y = EWG on the degree of bond breaking is normally in line with those predicted by the E_{pl} term, the C*-L bond loosening effect predicted by the E_{ct} term being a special case for the strongly antibonding C*-L bond with a good leaving group L.

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14. Our MNDO calculations on systems CH_3COOCH_2Cl and $CH_3OSO_2C_6H_4Cl$ showed that the LUMO level is lower and the AO coefficients of the antibonding LUMO for the two leaving atoms are larger for the latter indicating that the OSO_2ØCl group is a much better leaving group than the OCH_2Cl group; the LUMO levels were 0.33 and 0.23 a.u. and the 2p-AO coefficient for the C*-O* in the

LUMO were 0.59, 0.15 and 0.58, 0.57 for OCH_2Cl and OSO_2OCl respectively.
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Crystal Structure of Fully Dehydrated Partially Ag^+-Exchanged Zeolite 4A, $Ag_{7.6}Na_{4.4}$-A. Ag^+ Ions Prefer 6-Ring Sites. One Ag^+ Ion is Reduced

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The structure of partially Ag^+-exchanged zeolite 4A, $Ag_{7.6}Na_{4.4}$-A, vacuum dehydrated at 370°C, has been determined by single-crystal x-ray diffraction techniques in the cubic space group, *Pm3m* (a = 12.311(1)Å) at 24(1)°C. The structure was refined to the final error indices $R_1 = R_2$ (weighted) = 0.064 using 266 independent reflections for which $I_o > 3\sigma(I_o)$. Three Na^+ ions occupy the 3 8-ring sites, and the remaining ions, 1.4 Na^+ and 6.6 Ag^+, fill the 8 6-ring sites; each Ag^+ ion is nearly in the [111] plane of its 3 O(3) ligands, and each Na^+ ion is 0.9Å from its corresponding plane, on the large-cavity side. One reduced silver atom per unit cell was found inside the sodalite unit. It was presumably formed from the reduction of a Ag^+ ion by an oxide ion of a residual water molecule or of the zeolite framework. It may be present as a hexasilver cluster in 1/6 of the sodalite units, or, most attractively among several alternatives, as an isolated Ag atom coordinated to 4 Ag ions in each sodalite unit to give $(Ag_5)^{4+}$, symmetry *4mm*.

Introduction

Ag^+ ions in zeolite A can be reduced by heating,[1,2] by reaction with reducing agents,[3] or by the sorption of metal atoms.[4] (Many reports of the reduction of Ag^+ by these methods in other zeolites can be found.) Recently the structures of dehydrated Ag_xNa_{12-x}-A treated with H_2 at room temperature and at 330°C were determined in an effort to learn more about the reduction of silver ions in partially Ag^+-exchanged zeolite A.[3,5] In the structure of dehydrated Ag_6Na_6-A[3,6] treated with 50 torr of H_2 at room temperature, 1.27 $(Ag_3)^+$ clusters and 0.7 $(Ag_3)^{2+}$ clusters per unit cell were found in the large cavity. In the structure of $Na_{7.4}Ag_{4.6}$-A, vacuum dehydrated and treated with H_2 at 350°C, $(Ag_6)^{3+}$ clusters were present in the large cavity.[5]

Schöller *et al.* investigated the influence of monovalent cations in different positions in zeolite 4A on the diffusivity of trans-2-butene.[7] They concluded that Ag^+ ions preferentially occupy 6-ring centers and that Na^+ ions prefer 8-ring sites.[8] Similar results were obtained by Nitta *et al.*,[9] who studied the site selectivity of Ag^+ ions in dehydrated Ag_8Na_4-A by calculating cation-lattice interaction energies and charge-transfer stabilization energies for Ag^+ and Na^+ cations in 6-ring and in 8-ring sites.

This work was done to determine the cation distribution crystallographically, to see whether complete dehydration of $Ag_{7.6}Na_{4.4}$-A could be achieved at 370°C without generating Ag atoms, and to learn the structure for comparison with others of similar composition evacuated at other temperatures or treated with H_2.