Transition State Geometries and the Magnitudes of S_N2 Barriers. A Theoretical Study

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For S_N2 reactions of the type $Y^- + MeX \rightarrow YMe + X^-$, there exist extended linear correlations between (i) the magnitude of the central barrier and the percentage elongation of the C–X bond in the transition state; (ii) the looseness of the transition state and the sum of the forward and reverse central barriers.

The search for relationships between transition state structures and experimental observables is an important aspect of physical organic chemistry. Two such relationships are of particular interest because of their extensive use by experimentalists. In the Bell–Evans–Polanyi–Leffler–Hammond postulate,[1] the 'earliness' of a transition state is related to the exoergicity of the reaction. In the contour diagram model,[2] the notion of a 'perpendicular effect' is added, which relates[2b,c] the looseness of a transition state to the stabilities of potential reaction intermediates. The present work is concerned with relationships between transition state structures and the magnitudes of reaction barriers. The barrier can, in turn, be related in various ways to the primary kinetic observable, the rate of the reaction. By use of *ab initio* computational data, it is shown that for S_N2 reactions of MeX molecules these relationships are linear, and extend over a range of *ca.* 80 kcal/mol (1 kcal = 4.184 kJ) in activation energies and *ca.* 70% in bond elongation. The generality of these relationships suggests that it should become possible to deduce the microscopic structure of an S_N2 transition state, directly from a single rate constant (barrier).

Computations[3] on identity S_N2 reactions (equation 1) have revealed that the looseness of the transition state correlates with the magnitude of the *central* barrier. Thus a larger barrier is associated with a transition state having a higher percentage of C–X bond lengthening. The State Correlation Diagram (SCD) model[3,4] explains the origins of such correlations.† The central ideas are that deformation of the MeX substrate is required to promote curve crossing,[3,4a] and that the resulting barrier height is proportional to this deformation.† The deformation is found to be dominated by the C–X stretching[3] which, in turn, determines the looseness of the transition state. A correlation between barrier height and looseness therefore appears to originate in the nature of the activation process itself.[3,4a]

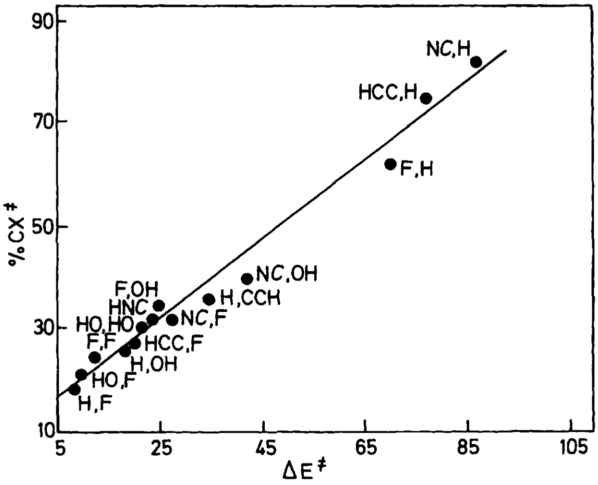

Figure 1. A plot of %CX‡ against the central barrier (kcal/mol) for the reaction $Y^- + MeX \rightarrow YMe + X^-$. The pairs Y, X are indicated by the data points (*e.g.*, HO, F signifies HO = Y, F = X, italic *C* indicates the site of attachment).

$$X^- + MeX \rightarrow XMe + X^- \quad (1)$$

Extension of the scope of such correlations to include reactions governed by the Bell–Evans–Polanyi–Leffler–Hammond postulate requires an examination of the forward and reverse central barriers and geometric features of non-identity reactions (equation 2), for which an extended set of data are available at the 4–31G level.[5,6] For the forward reaction (equation 2), the percentage elongation of the C–X bond, as between the reactant ion–molecule complex (with bond length d^0 in the molecule)[3] and the transition state (with bond length $d^{\ddagger}$), is given by equation 3a; the corresponding expression for the percentage elongation of the C–Y bond for the reverse reaction is equation 3b.

$$Y^- + MeX \underset{\Delta E_r^{\ddagger}}{\overset{\Delta E_f^{\ddagger}}{\rightleftharpoons}} YMe + X^- \quad (2)$$

$$\%CX^{\ddagger} = 100\,(d^{\ddagger}_{CX} - d^0_{CX})/d^0_{CX} \quad (3a)$$

$$\%CY^{\ddagger} = 100\,(d^{\ddagger}_{CY} - d^0_{CY})/d^0_{CY} \quad (3b)$$

Figure 1 shows a plot of %CX‡ *versus* the central barriers $\Delta E^{\ddagger}$ for 14 S_N2 reactions (out of 30). The plot encompasses thermoneutral, exoergic, and endoergic reactions, which span a range of *ca.* 80 kcal/mol in activation energies and *ca.* 70% in bond stretching. The correlation is seen to be linear (r = 0.992; for the entire data set r = 0.985), and it follows that the higher the S_N2 barriers, the more extensive is the bond cleavage of the leaving group in the transition state, *i.e.*, equations 4 and 5. In turn, defining the looseness of the transition state as $L^{\ddagger} = \%CX^{\ddagger} + \%CY^{\ddagger}$, it can be seen that the *sum* of equations 4 and 5 predicts a correlation of looseness with the sum of the barriers for the forward and reverse reactions (equation 6).

$$\%CX^{\ddagger} = a\Delta E_f^{\ddagger} + b \quad (4)$$

$$\%CY^{\ddagger} = a\Delta E_r^{\ddagger} + b \quad (5)$$

$$L^{\ddagger} = (\%CX^{\ddagger} + \%CY^{\ddagger}) = a\,(\Delta E_f^{\ddagger} + \Delta E_r^{\ddagger}) + 2b \quad (6)$$

Figure 2 shows a plot of $L^{\ddagger}$ *versus* the sum of the barriers, $(\Delta E_f^{\ddagger} + \Delta E_r^{\ddagger})$. This plot contains variations of X and Y across the Periodic Table, and its linearity (r = 0.975) means that the geometric looseness of the transition state increases with

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† In the general case, gas phase barriers derive from deformations and nonbonded repulsions.

increase in the sum of the forward and reverse barriers. These correlations can be related to existing structure–reactivity concepts.[1,2] Thus, the difference between equations 4 and 5 leads to equation 7. It is seen that the reaction exoergicity (ΔE^0) determines the degree of asymmetry of the transition state. Equation 7 appears similar to the Bell–Evans–Polanyi–Leffler–Hammond principle.[1] It should be noted however, that rate–equilibrium relationships generally break down for this set of S_N2 reactions (*e.g.*, see Figure 1: identity reactions possess much smaller barriers than exothermic reactions).[6b,7a] Thus, equation 7 is valid despite the general invalidity of rate–equilibrium relationships and not because of them.

$$\%\mathrm{CX}^\ddagger - \%\mathrm{CY}^\ddagger = a(\Delta E_f^\ddagger - \Delta E_r^\ddagger) = a\Delta E^0 \qquad (7)$$

The relationship to the contour diagram model[2] is less obvious because, in the gas phase, the intermediate corner $Y^-/Me^+/Y^-$ is too high to influence the looseness of the transition state.[7b] Nevertheless, a significant 'perpendicular effect' is apparent in Figure 2, as some thermoneutral reactions are seen to possess looser transition states than exoergic reactions. These 'perpendicular effects' are dominated by the increasing sum of the forward and reverse barriers; thus reflecting the activation effort.[3,4a] Remarkably extended linear correlations emerge between barriers and transition state geometries. These correlations reflect the nature of the activation process, by showing that the establishment of an S_N2 transition state requires predominantly bond stretching. Furthermore, it is this particular deformation which is the primary contributor to the barrier.[3,4a]

The relationships between barrier heights and transition state geometries have recently been given a thermochemical foundation,[8] which shows that the larger the barrier the closer is the transition state to its dissociation limit (the three isolated fragments). Thus, the correlation reported in this Communication does not appear to be an accidental artifact of the 4–31G basis set but rather a physically reasonable link.[†] Nevertheless, higher level basis sets,[‡] as well as other methods,[§¶] will still be required to establish whether the correlation is not only qualitative but also *linear* as suggested by the present analysis of the 4–31G data, and whether the relation is global or confined to certain related S_N2 families. Since the looseness of transition state, of the type $(YMeX)^{-\ddagger}$, appears to be marginally affected by solvation,[12] then an affirmation of the above linear relationships may be useful in deducing the structure of the transition state for S_N2 reactions in solution.

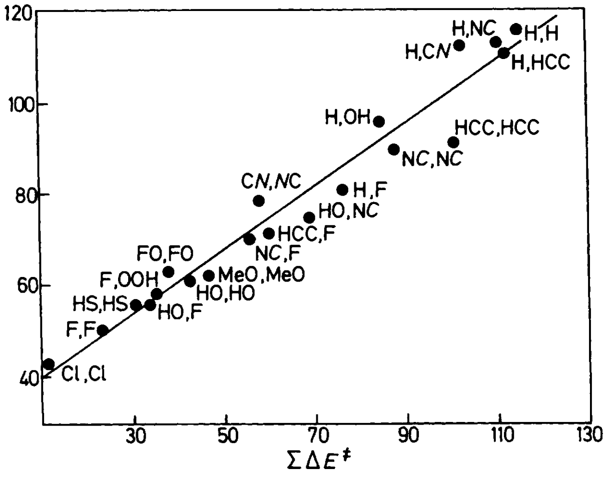

Figure 2. A plot of transition state looseness, $L^\ddagger$, against the sum of the central barriers, $\Sigma\Delta E^\ddagger = (\Delta E_r^\ddagger + \Delta E_f^\ddagger)$, for $Y^- + MeX \rightarrow YMe + X^-$ (each point with $X \neq Y$ involves two barrier data, italic *C* and *N* indicate the site of attachment).

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[‡] Results of higher basis sets exist for the identity reactions of H^-, F^-, and Cl^-. The barriers follow the same order as in the 4–31G basis set. The largest percentage elongation is computed for the reaction of H^- [refs. 9(a—c)], while the percentage elongations for the reactions of F^- and Cl^- appear to be inverted in one study.[9c]

[§] Results with the 3–21G basis set[10a,b] show the same order of barriers and percentages of elongation, as with the 4–31G basis set, for the reactions of F^- and Cl^-. MNDO and AM1 results[10c,d] show a correlation of barriers and percentages of elongation for the reactions of F^-, Cl^-, Br^-, and I^-.

[¶] Gas phase identity barriers, available from Rice-Ramperger-Kassel-Marcus (RRKM) and Marcus equation analyses,[11a,b] show trends in agreement with the 4–31G barriers with one exception. Thus, the gas phase barrier of F^- is larger than that of MeS^-, while theory predicts a higher barrier for HS^- relative to F^-. It appears that the gas phase barrier of F^- is somewhat overestimated. Estimates from experimental data and the best theoretical calculations all give a barrier of *ca.* 19—20 kcal/mol for F^-,[9a,11c] so that the final order may still agree with the theoretical prediction.

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