



increase in the sum of the forward and reverse barriers. These correlations can be related to existing structure–reactivity concepts.<sup>1,2</sup> Thus, the difference between equations 4 and 5 leads to equation 7. It is seen that the reaction exoergicity ( $\Delta E^0$ ) determines the degree of asymmetry of the transition state. Equation 7 appears similar to the Bell–Evans–Polanyi–Leffler–Hammond principle.<sup>1</sup> 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).<sup>6b,7a</sup> Thus, equation 7 is valid despite the general invalidity of rate–equilibrium relationships and not because of them.

$$\%CX^\ddagger - \%CY^\ddagger = a(\Delta E_f^\ddagger - \Delta E_r^\ddagger) = a\Delta E^0 \quad (7)$$

The relationship to the contour diagram model<sup>12</sup> 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.<sup>7b</sup> 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.<sup>3,4a</sup> 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.<sup>3,4a</sup>

The relationships between barrier heights and transition state geometries have recently been given a thermochemical foundation,<sup>8</sup> 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.<sup>†</sup> Nevertheless, higher level basis sets,<sup>‡</sup> as well as other methods,<sup>§¶</sup> 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,<sup>12</sup> 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.

† 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.<sup>9c</sup>

§ Results with the 3–21G basis set<sup>10a,b</sup> 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<sup>10c,d</sup> 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–Rampenger–Kassel–Marcus (RRKM) and Marcus equation analyses,<sup>11a,b</sup> 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  $F^-$ .<sup>9a,11c</sup> so that the final order may still agree with the theoretical prediction.

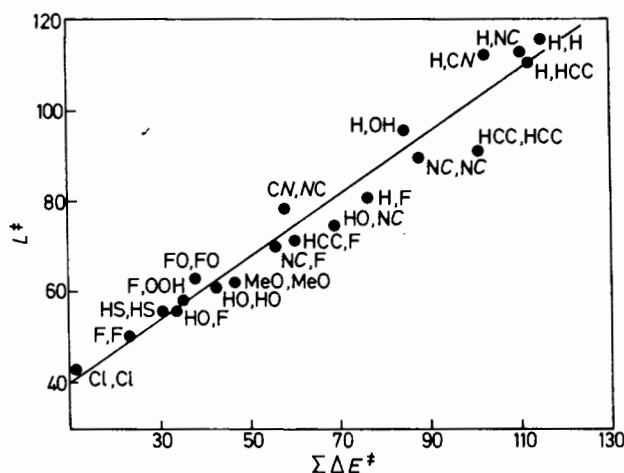


Figure 2. A plot of transition state looseness,  $L^\ddagger$ , against the sum of the central barriers,  $\Sigma\Delta E^\ddagger \doteq (\Delta E_f^\ddagger + \Delta E_r^\ddagger)$ , for  $Y^- + MeX \rightarrow YMe + X^-$  (each point with  $X \neq Y$  involves two barrier data, italic C and N indicate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

We thank the Natural Sciences and Engineering Research Council of Canada for an International Scientific Exchange Award (to S. S. S.). Helpful discussions with Professor J. M. Harris and critical readings by Professor A. Pross are also acknowledged.

Received, 7th December 1987;|| Com. 7/00016B

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|| Received in revised form 23rd May 1988 (1987 Com. 1753).