

### CUBIC REACTION COORDINATE DIAGRAM IN THE NUCLEOPHILIC SUBSTITUTION PROCESS

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**ABSTRACT:** A three-dimensional diagram obtained from the More O'Ferrall plot by the addition of one more perpendicular coordinate reflecting the biradicaloid character of the transition state is proposed for analysis of  $S_N2$  reactions.

The More O'Ferrall diagram has been widely applied for the qualitative determination of energy barriers and the transition state position in  $S_N2$  reactions [1]. Nevertheless this diagram lacks an explanation for the nucleophile dependence on the ionization potentials [2a], the  $\alpha$ -effect [2b], different reactivity of nucleophiles with the same basicity [2c], and some other effects.

The purpose of this communication is to present a multi-dimensional diagram which is capable of explaining many features of  $S_N2$  reactions. This new diagram can be drawn by the addition of one more perpendicular coordinate to the More O'Ferrall plot. The new coordinate reflects the biradicaloid character of the transition state (Figure 1). The transition state position along the reaction coordinate (1-3 diagonal) is qualitatively determined with the Hammond postulate [3], and along the perpendicular coordinates 2-4 and 5-6 with the Thornton's rule [4]. In other words, if the state  $(Y \cdot R \cdot X)$  has lower energy than  $(Y : R \cdot X)$ , it makes a greater contribution to the transition state because of the more pronounced dependence of  $\Delta G^\ddagger$  on the energy of transformation of the reagents to  $(Y \cdot R \cdot X)$ .

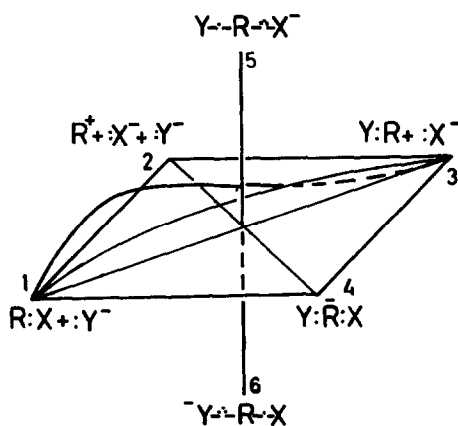


Figure 1. The More O'Ferrall plot with additional perpendicular coordinate.

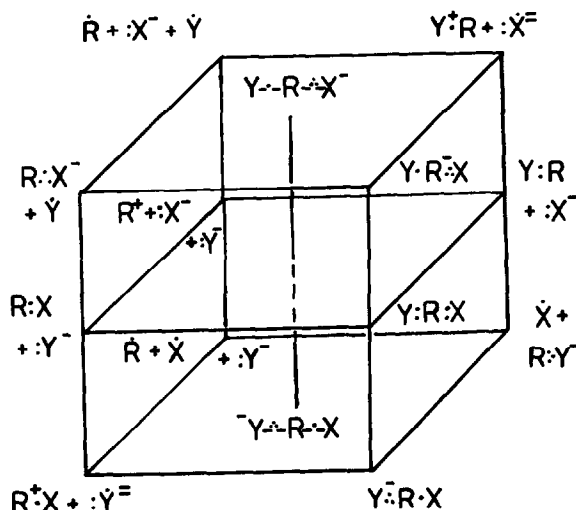


Figure 2. Cubic reaction coordinate diagram for  $S_N2$  reactions.

In contrast to the More O'Ferrall plot in which the  $\Delta G^\ddagger$  is a function of the diagram's four corners relative energies [5], in our model the energy barrier depends also on the energies of states  $\underline{5}$  and  $\underline{6}$  in the diagram (Figure 1). Unfortunately, the experimental determination of these energies is impossible. However, application of an extended three dimensional diagram (Figure 2) solves this problem. It can be seen from Figure 2 that the  $\Delta G^\ddagger$  depends not only on the nucleophile and the leaving group affinity to the  $R^+$ , but also on their ionization potentials, substrate RX and product RY electron affinities, and other factors.

We will consider as an example the cubic diagram application for explanation of the  $\alpha$ -effect. Thus, the methyl cation affinity of the hydroperoxide anion is slightly lower than that of the hydroxide anion (272.6 and 276.3 kcal/mol correspondingly) [6], but its reactivity is much higher both in the gas phase [7], and solution [8]. The similar methyl cation affinity of both anions results in close energies for the four corners at the More O'Ferrall plot presentation of their reaction with  $CH_3X$ . That is why the higher reactivity of  $HO_2^-$  can be explained with lower energy of states  $(Y \cdot R \cdot \cdot X)$  and/or  $(Y \cdot \cdot R \cdot X)$  in reactions of  $HO_2^-$  in comparison with  $HO^-$ . The relatively low ionization potential and the high polarizability of the hydroperoxide anion stabilize these states in comparison with the reactions of hydroxide anion, and cause the observed differences in reactivity of the anions.

The increase in polarizability of the nucleophiles from the third and subsequent rows in the Periodic Table causes a relative stabilization of the states  $(Y \cdot R \cdot \cdot X)$  and  $(Y \cdot \cdot R \cdot X)$  in comparison with the same states for the nucleophiles of the second row. Thus our approach gives a visual explanation why nucleophiles with a similar basicity, such as alcohols, thiols, and selenols, show appreciable differences in reactivity.

The three-dimensional diagram can be applied for the explanation of the superweak nucleophilicity of perchlorate and sulfonate anions in comparison with the iodide anion, which also shows low basicity, but is a good nucleophile. Iodide anion is a very polarizable anion, and  $ClO_4^-$  is one of the hardest among the nucleophiles. The great difference in energy of the states  $(Y \cdot R \cdot \cdot X)$  and  $(Y \cdot \cdot R \cdot X)$  thus leads to such a difference in nucleophilicity for these anions.

Analogous n-dimensional diagrams can be applied for the explanation of unusual kinetic effects in different reactions such as: polar effects in radical reactions; substrate and position selectivities in aromatic substitution; dependence of alkene reactivity in  $Ad_E$  reactions on their ionization potentials, etc.

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### References

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