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The structural stability restriction rules out certain frontside S_N2 pathways

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The S_N2 reactions are known to proceed invariably with inversion of configuration (for an account see Ref. 1). However, we have noticed that certain nucleophile frontside attack pathways cannot be ruled out on the basis of being energetically less favorable than the usual backside attack. The principle of structural stability of adiabatic potential energy surfaces (APES) must be taken into account. This principle was introduced by A. Fernández and O. Sinanoğlu in a number of papers [2, 3].

To apply this principle, we have selected an S_N2 whose energetics were extensively studied with *ab initio* methods by a number of people, among them, Schlegel and Mislow considered all possible *a priori* paths ([4] and references therein). The relative stabilities of the transition states for frontside and backside attack are tabulated elsewhere [4, 5]. The reaction considered is the S_N2 between $F^-_{(a)}$ and $CH_3F_{(b)}$.

1. Unsuccessful frontside attack path coupled to the usual backside path

The backside attack leading to the Walden inversion presents an intermediate species which is a minimum in the APES and it corresponds to a $F^-_{(a)}-CH_3F_{(b)}$ cluster with C_{3v} symmetry [4].

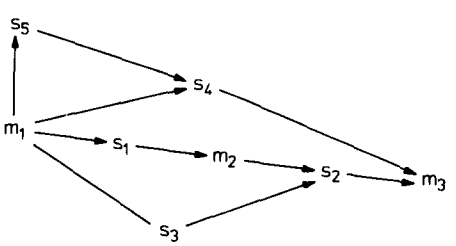


Fig. 1. Structurally unstable model of the S_N2

The process is represented:

$$m_1 \dashrightarrow s_1 \dashrightarrow m_2 \dashrightarrow s_2 \dashrightarrow m_3$$

Where:

$m_1 = F^-_{(a)} + CH_3F_{(b)}$

$m_3 = F_{(a)}CH_3 + F^-_{(b)}$

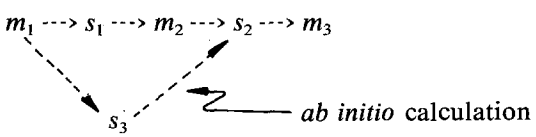
$m_2 = C_{3v}$ cluster

$s_2 = D_{3h}$ transition state

$\dashrightarrow$ = Intrinsic reaction coordinate path [6].

The m_i's are minima and the s_j's transition states in the APES. Or, respectively, sinks and saddles of the gradient field of the APES [2, 3].

Now consider the frontside attack along a 2H edge in a HCF plane [4]. This path leads to a critical configuration s_3 which is a C_{2V} trigonal bypiramid. The *ab initio* calculations show [4] that this configuration relaxes to the optimum configuration s_2.



We shall now show that the second path cannot be successful since s_3 cannot be a transition state configuration. If it were, there would be an integral curve of the gradient field of the APES (the calculated relaxation $s_3 \dashrightarrow s_2$) joining two saddles without passing through any intermediate critical point. This saddle-saddle connection implies that the APES is structurally unstable as it was demonstrated by these authors in paper 2. Therefore s_3 must be a maximum in 2 of the 12 degrees of freedom

2. Unsuccessful frontside attack path coupled to the path of minimum energy for the retention of configuration

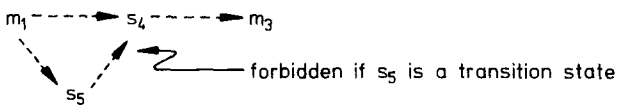
Stohrer proposed a transition state configuration for the S_N2 with retention of configuration [7]. This path is more endothermic than the backside attack:

$$m_1 \dashrightarrow s_4 \dashrightarrow m_3$$

s_4 = Stohrer's transition state.

Now consider the path of attack along the HF edge in a HCF plane. This leads to a C_s-trigonal bypiramid denoted here s_5. This pathway is unsuccessful; as shown by an analogous analysis: s_5 does not correspond to a transition state but to a maximum. We shall prove this by using again the principle of structural stability.

The imput data is the fact that s_5 relaxes to the optimum configuration s_4. This fact was proven by *ab initio* methods by Schlegel and Mislow [4].



If s_5 were a transition state configuration, then, again, there would be a saddle-saddle connection but the existence of such an integral curve is precluded by the principle of structural stability of APES.

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