Unexpected Bond Order Relationships in Extremely 'Loose' S_N2 Transition States

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According to MNDO semi-empirical molecular orbital calculations, the transition state structures for S_N2 reactions where the corresponding S_N1 processes take place very readily are dominated by *anti*-Hammond effects, in contrast to the normal Hammond behaviour predicted for typical S_N2 reactions.

That variations in transition state structure can be related to reactant structure is central to much mechanistic argument.[1] According to the familiar Hammond postulate,[2] such variations are seen as displacements along a one-dimensional reaction co-ordinate spanning extremes of reactant- and product-like structures. These expectations for typical S_N2 reactions are borne out by both *ab initio*,[3] and semi-empirical MNDO[4] molecular orbital calculations.

However, we have uncovered a group of S_N2 reactions which, according to our MNDO calculations,[5] behave in a different, and quite unexpected way. For these reactions (displacement of N_2 from alkanediazonium ions and ring-opening of protonated oxiranes) the corresponding S_N1 processes are extremely facile and the bimolecular transition states therefore very 'loose'.[6] Here, the bond orders[7] of the forming and breaking bonds in the calculated transition states (Figure 1) are correlated with *positive* slopes. Thus a decrease in the length of the forming bond (increase in bond order) implies a parallel *decrease* in the length of the breaking bond. In contrast, the published[4] MNDO data for a typical S_N2 reaction, the displacement of Br^- from MeBr, lead to the expected negative slope (−1.01) corresponding to 'normal' Hammond behaviour.

In terms of the analysis developed by Thornton[8] and others,[9] the '*anti*-Hammond'[1] behaviour predicted for the present reactions corresponds to displacement of the transition structures in directions perpendicular[8,10,11] to the reaction co-ordinate. The unexpected dominance of such effects here is associated with the unusually low curvatures† of the potential energy surfaces in this direction,[6,12] an effect which is probably quite general for reactions involving very loose transition states.

The slopes of the correlation lines themselves (Figure 1) are indicative of the extent of nucleophilic participation in the transition states. N_2 loss from the ethanediazonium ion, the reaction for which the corresponding S_N1 barrier is least, exhibits the smallest slope. Higher values are obtained for the less facile ring-opening reactions. The methanediazonium ion, for which unimolecular nitrogen loss is surprisingly endothermic,[6,13] represents an interesting borderline case. The two oxygen nucleophiles (Figure 1) conform to the behaviour

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† This is shown, for example, by the very low frequencies calculated (100—150 cm^{-1}) for the bound vibrational modes corresponding to displacement in this direction.

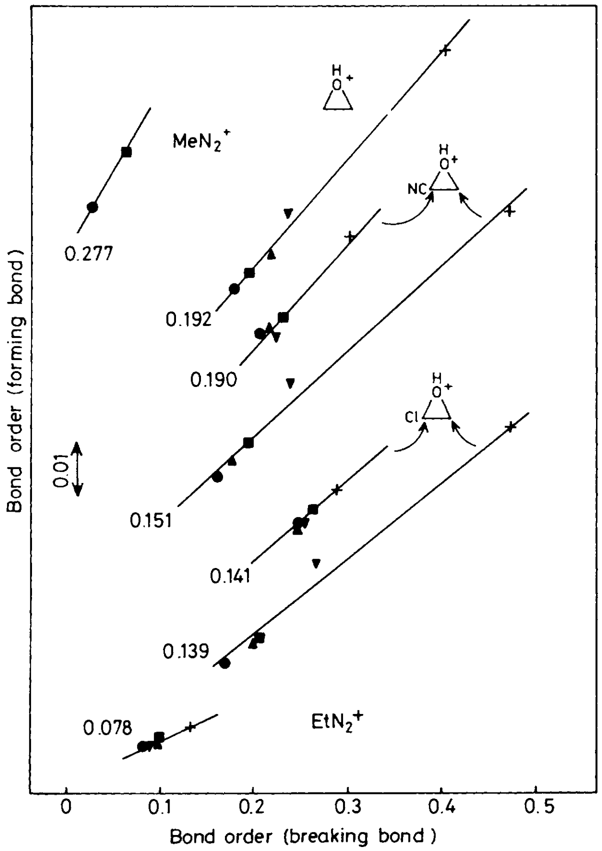

Figure 1. Bond order of the forming *vs.* bond order of the breaking bond in the calculated transition states for nucleophilic attack of water (●), formamide (O attack) (■), methylamine (▲), pyrimidine (▼), and imidazole (+) on the substrates indicated. The slopes of the regression lines (arbitrarily displaced in the vertical direction for clarity) are shown to the left of each. Bond orders calculated from the Pauling relationship:[7] $n = \exp\{(r_0 - r^{\ddagger})/0.26\}$, where $r^{\ddagger}$ is the calculated (MNDO) distance in the transition state and r_o the corresponding length in the reactant or product from refs. 6, 12, and unpublished work by the authors. Similar but less precise correlations result using bond orders based on the MNDO density matrices or the APS[14] partitioning scheme.

discussed above, with the larger slope indicative of a more S_N2-like process. However, for the stronger nitrogen nucleophiles the system reverts to that expected for typical S_N2 behaviour with these defining a separate line (not shown) of slope −0.267.

We thank the National Institutes of Health (U.S.A.) for financial support for this research and the SMU Computer Center for a generous allocation of computer time. The H800 minicomputer used for many of the calculations was a gift from the Harris Corporation to the SMU Department of Civil and Mechanical Engineering.

Received, 31st July 1986; Com. 1098

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