Theoretical Evaluation of Kinetic Stereoelectronic Effects on Hydride Transfer

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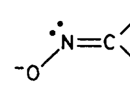
Ab initio calculations for hydride transfer from $HNCH_2$ to $HCNH^+$ with full optimisation at the MP2/6-311G** level predict that orientation of nitrogen lone pairs antiperiplanar to the transition-state C · · · H bonds lowers the reaction barrier by 22 kJ mol^{-1}, but that a quasi-cyclic transition structure with synperiplanar lone pairs is even more favourable, being lower in energy by another 46 kJ mol^{-1}.

Critical evaluation of the kinetic rôle of suitably oriented electronic lone pairs upon bond-making/breaking processes is often complicated by the presence of stereoelectronic effects on the conformational energetics of the reagents(s). While there is a wealth of experimental data and theoretical results in support of the view that lone pairs antiperiplanar to polar bonds are stabilising structural features for molecules at equilibrium[1] (*i.e.* thermodynamic stereoelectronic effects), the evidence for such interactions occurring in transition states (*i.e.* kinetic stereoelectronic effects) has not been generally convincing,[2] despite the popularity of the notion.[3] Perhaps the first clear experimental demonstration of a kinetic stereoelec-



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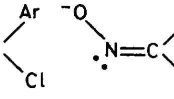

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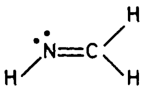

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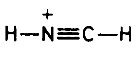

$H-\overset{+}{N}\equiv C-H$

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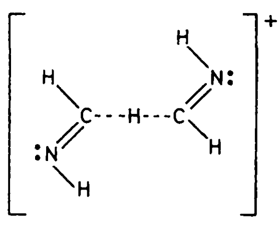

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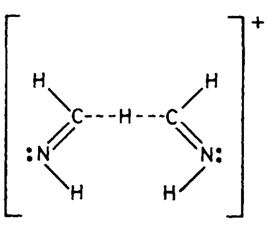

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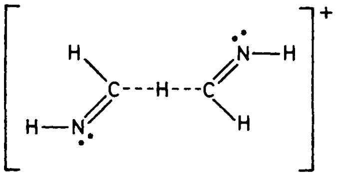

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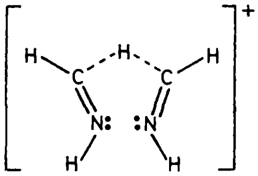

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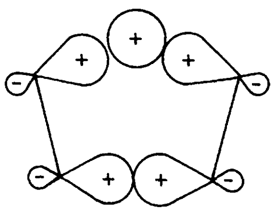

Figure 1. The in-plane orbitals involved in bond making and bond breaking.

tronic effect was the >10^7-fold enhancement[4] in the rate of chloride ion elimination from (**1**) as from (**2**); even so, evaluation of the transition-state energetic stabilisation would require a quantitative knowledge of the energy difference between the reagent isomers. We now report theoretical results which provide unambiguous estimates of kinetic stereoelectronic effects on the symmetrical transfer of hydride ion from methylenimine (**3**) to formonitrilium cation (**4**). This model reaction is stereoelectronically well-defined, and consideration of its transition-state energetics is not complicated by reagent-state contributions.

Full geometry optimisation (within C_{2h} or C_{2v} symmetry) has been performed for the hydride-transfer transition structures (**5**)—(**8**) at various levels of *ab initio* M.O. theory;[5] potential energies of these first- or second-order saddle-point structures relative to the separated reagents are given in Table 1.

Structures (**5**) and (**6**) both have nitrogen lone pairs antiperiplanar to the transferring hydride but differ in their overall geometry. An energetic comparison of the *trans*-structure (**5**) with the *cis*-structure (**6**) reveals notably little geometrical preference; the *trans* geometry is very slightly favoured at all levels of S.C.F. theory. The C · · · H · · · C angle in (**5**) is 180° by symmetry, but in (**6**), where it is not constrained by symmetry, this angle is also remarkably close to 180° (178.8° at HF/6-31G*).

Structures (**5**) and (**7**) both possess *trans* geometry but differ in their lone-pair orientations. The MP2/6-311G** method (with electron correlation included by second-order perturbation theory, using an extensive basis set) predicts the antiperiplanar lone-pair structure (**5**) to be 22 kJ mol^{-1} lower in energy than the synperiplanar lone-pair structure (**7**). The energies of the reagents are identically the same in each case, and there are no other complications (such as steric interactions) affecting the relative energies of these transition structures. The energetic difference is purely a kinetic stereoelectronic effect corresponding to a rate enhancement (at 298 K) of ~6.5×10^3 in favour of antiperiplanar lone pairs. Interestingly, however, S.C.F. calculations with the 3-21G and 6-31G* bases fail to describe this stereoelectronic effect; indeed they predict a small effect in the opposite direction.

Table 1. Calculated energies (kJ mol^{-1}) for optimised hydride-transfer transition structures (first- or second-order saddle points) relative to separated reagents.

Method	Transition structure			
	(**5**)	(**6**)	(**7**)	(**8**)
3-21G	160	164	156	128
6-31G*	165	167	157	147
MP2/6-311G**	72	—	94	26

At first sight structure (**8**) appears to have the wrong overall geometry (*cis*) and the wrong stereoelectronics (both lone pairs synperiplanar). Nonetheless, at all levels of theory employed this is the lowest-energy transition structure (a similar result has recently been reported for hydride transfer from methylamine to methyleniminium cation;[6] this system is stereoelectronically less well-defined than the present one, owing to the ease of inversion at NH_2). The MP2/6-311G** optimised geometry for this species shows a C · · · H · · · C angle of 135° and a N · · · N distance of only 2.15 Å. We suggest that the surprising stability of this quasi-cyclic transition structure reflects a degree of aromaticity: the in-plane orbitals involved in bond making and breaking (Figure 1) are isoconjugate with the π-orbitals of cyclopentadienyl anion, another 5-centre 6-electron system with Hückel topology. The energetic difference between (**7**) and (**8**) yields the extent of aromatic stabilisation as 68 kJ mol^{-1}.

These results confirm the general validity of the notion of assistance to bond making and breaking by antiperiplanar lone pairs, but suggest the need to include electron correlation in theoretical descriptions of stereoelectronic effects. Furthermore, the possibility of 'anti-Deslongchamps' stereoelectronic effects involving specific orbital interactions is demonstrated. A full account of other interesting features of the potential-energy surface for this most informative model reaction will be presented in due course.

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