

Isotope Effects in *E2* Transition States with Non-linear Proton Abstraction

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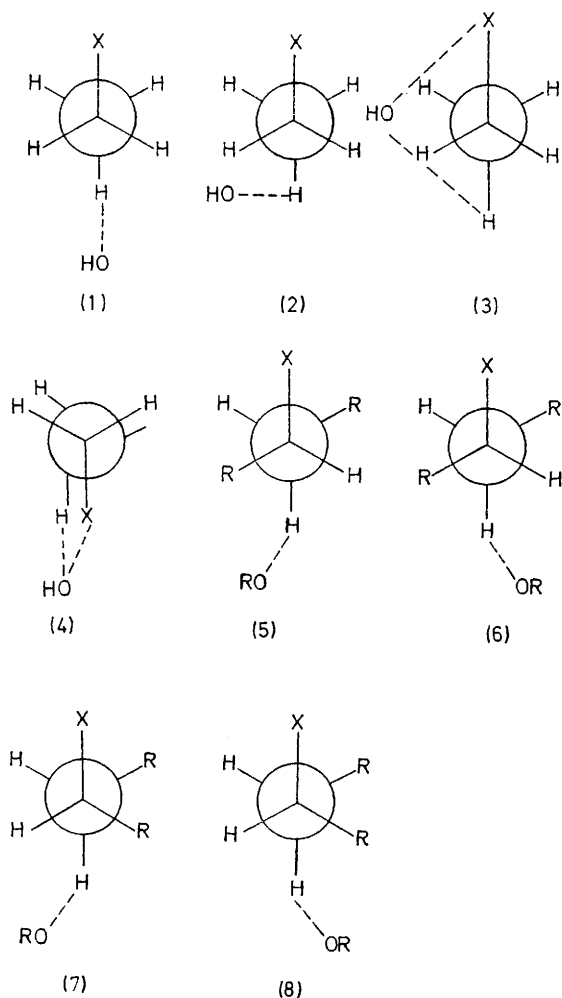
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Summary Calculations show that *E2* transition states in which the base, β -hydrogen, and β -carbon forms a right or acute angle give β -deuterium isotope effects substantially smaller than those normally found experimentally.

A RECENT paper offers an explanation of stereochemistry and *trans/cis* product ratios in bimolecular (*E2*) eliminations based on electrostatic interactions between base and leaving groups.¹ These models involve marked departures from the linear arrangement normally assumed for the base, β -hydrogen, and β -carbon, especially in the case of *anti* eliminations. The authors recognize that hydrogen isotope effects are expected to be lower for non-linear than linear proton transfers,² but argue that variations in the extent of

entirely true, their hypothesis still requires that k_H/k_D for the non-linear transition states at least have *maximum* values consistent with those observed for known *anti* eliminations.

In order to determine whether this requirement is fulfilled by transition-state models like those of Závada, *et al.*,¹ calculations were carried out on k_H/k_D for the transition states (1)–(4) using the Wolfsberg–Stern program³ based on the FG-matrix method.⁴ The procedures of calculation and the main features of the models followed our earlier work.^{5,6} The leaving group, X, had the mass and the C–X



proton transfer in different transition states make it "unwarranted to expect in the present case any simple relationship between the transition-state geometry and magnitude of the isotope effect." While this statement is

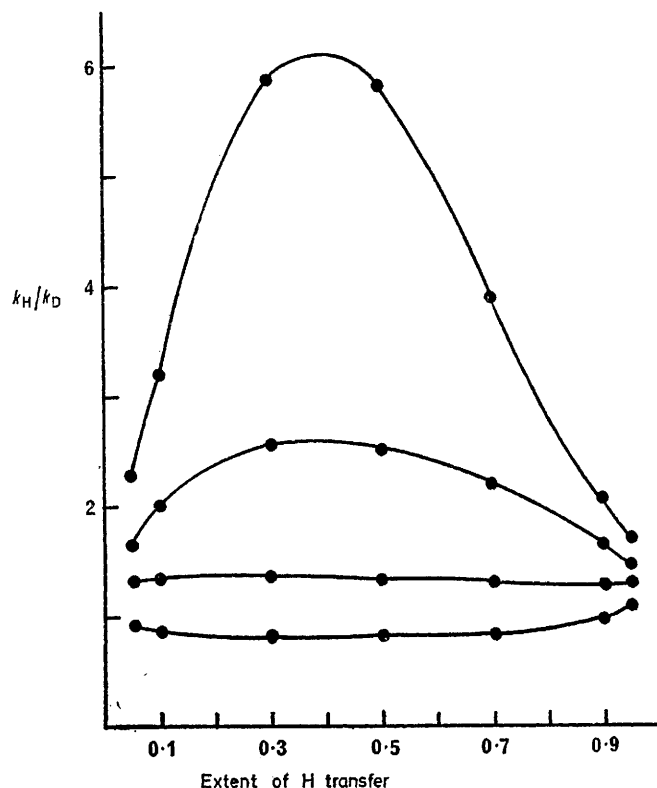


FIGURE. Calculated deuterium isotope effects at 25°C for full-bond models (see text) of elimination reaction. The calculated values (solid circles) are connected by arbitrary smooth curves. The curves represent, top to bottom, models (1), (4), (2), and (3), respectively.

bond the length appropriate for bromine, but the exact nature of the leaving group has very little effect on k_H/k_D . The O–H–C angle is 90° in (2), and the O–H bond is normal to a plane defined by H–C–C–X. In (3), a line from oxygen to the midpoint of the C–C bond is normal to the same plane. In (4) the oxygen is in that plane and the O–H–C angle is 120°. Thus, (4) represents a *syn* elimination, while (2) and (3) simulate the models of Závada, *et al.*,¹ for *anti* elimination with ion-paired and non-ion-paired base, respectively. The metal ion is omitted from (2) because the force field holding

it should be weak, and should consequently have little effect on k_H/k_D .

The k_H/k_D values from the calculations are plotted in the Figure as functions of the extent of hydrogen transfer in the transition state. This model, which is referred to as the full-bond model, assumes that total bonding to hydrogen remains constant (*i.e.*, at half transfer the C-H and O-H force constants are half their normal values, and the O-H-C bend is treated as before⁵). The full bond model (1) gives a maximum isotope effect in the range normally found for *anti* eliminations (for 2-phenylethyl derivatives at 30°, some typical k_H/k_D values for two leaving groups run: OTs with EtOK-EtOH 5.7; OTs with Bu^tOK-Bu^tOH, 8.0; NMe₃⁺ with EtOK-EtOH, 3.0 (50°); NMe₃⁺ with Bu^tOK-Bu^tOH, 7.0).⁷ The full-bond models (2) and (3) are clearly inconsistent with nearly all observed isotope effects for *E2* reactions. The full-bond model (4), on the other hand, is consistent with the relatively small isotope effects usually found in *syn* eliminations.^{7,8}

Another set of calculations was performed on a half-bond model, in which force constants involving bending and stretching motions of the transferred hydrogen were allowed to decrease to one-half of their values in the full-bond model at the point of half transfer. The half-bond model gives uniformly larger isotope effects than the full-bond model, the major factor presumably being the weaker O-H-C bend of the former. The maximum k_H/k_D values of 9.9 for the half-bond model (1) and 5.5 for (4) are somewhat larger than normally observed for *anti* and *syn* eliminations, respectively.^{7,8} The maximum values of 3.9 for (2) and 2.7 for (3) in the half-bond model are still lower than many reported values for *anti* eliminations,⁷ though consistent with some.

In summary, transition-state models for *anti* elimination with the extent of non-linearity of the B-H-C system

proposed by Závada, *et al.*, cannot be made consistent with observed isotope effects unless one assumes that the total bonding to the β -proton in the transition state is less than half that of a normal covalent bond. It seems unlikely that so much covalent bond energy would be sacrificed, so that these models can probably be rejected. On the other hand, the more modest degree of nonlinearity required for a *syn* elimination to take advantage of electrostatic interaction between the base and leaving group is not at all inconsistent with observed isotope effects.

Although only a linear or slightly non-linear B-H-C system seems consistent with observed *anti*-elimination isotope effects, a modified electrostatic model may still account for observed *trans/cis* ratios. In (5) and (6) (*trans*-olefin product), electrostatic interactions between oxygen and X must operate in part through solvent and in part through substrate skeleton. For the two transition states giving *cis*-olefin, the interactions operate nearly entirely through substrate skeleton in (8), but to some extent through solvent in (7). Electrostatic interactions depend inversely on the dielectric constant of the medium, and should be more powerful in (8) than in (5) or (6), so that an attractive interaction (RO negative, X positive) would favour *cis*-olefin, as observed.¹ Analogous arguments could be presented where X is a neutral group such as halide or tosylate, and the base is associated with a metal ion which may interact with X. This hypothesis differs from that of Závada, *et al.*¹ in that the base does not avoid alkyl group congestion in the substrate, but actually seeks it out as providing the most favourable medium of conduction for its interaction with the leaving group.

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