JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 20
1991

A Theoretical Comparison of Primary Deuterium Kinetic Isotope Effects in Analogous Hydride and Hydron Transfer Processes

Ann E. Pain and Ian H. Williams*

School of Chemistry, University of Bath, Bath BA2 7AY, UK

The semiclassical primary deuterium kinetic isotope effect (3.30 at 298 K) for symmetrical hydride transfer from HN=CH$_2$ to HC≡NH$^+$, computed at the HF/3-21G level of *ab initio* molecular orbital (MO) theory, is smaller than that for analogous proton transfer from HN=CH$_2$ to $^-$HC=NH (4.38) owing to extensive participation in the reaction-coordinate vibrational mode of degrees of freedom other than asymmetric C···H stretching.

Several reasons have been proposed to account for primary deuterium kinetic isotope effects (PDKIEs) of less than ~7 for hydrogen (H$^+$, H$^\cdot$ or H$^-$) transfer processes: (*i*) an unsymmetrical transition state (TS);[1] (*ii*) a non-linear TS;[2] (*iii*) the influence of bending vibrations in the TS;[3] (*iv*) the coupling of hydrogen and heavy-atom motions in the reaction coordinate.[3,4] PDKIEs for hydride-transfer tend to be small (typically ~3) even at the maximum value corresponding to a half-transferred hydride in the TS.[5] The usual conclusion is that hydride transfer prefers a bent TS, even for intermolecular reactions. A problem in directly comparing the magnitudes of PDKIEs for hydride-transfer (HT) processes with those for proton-transfer (PT, although more properly hydron-transfer) processes is to find analogous reactions which differ only in the number of electrons involved in the making and breaking bonds: two electrons for HT, four electrons for PT.[6] We now report the results of *ab initio* HF/3-21G MO calculations of PDKIEs for the pair of symmetrical reactions (1) and (2), which to our knowledge represents the first example of such a comparison between HT and PT.

$$\text{HT: HN=CH}_2 + \text{HC≡NH}^+ \rightarrow {}^+\text{HN≡CH} + \text{CH}_2\text{=NH} \quad (1)$$
$$\text{PT: HN=CH}_2 + {}^-\text{HC=NH} \rightarrow \text{HN=CH}^- + \text{CH}_2\text{=NH} \quad (2)$$

We have previously reported the relative energetics of four different symmetrical TS structures for reaction (1) at this and higher levels of theory;[7] the lowest-energy TS is a quasi-cyclic structure with five-centre six-electron stabilisation involving σ lone pairs on the heteroatoms (*cf.* ref. 8). In order to provide for the most meaningful comparison of PDKIEs for reactions (1) and (2), the TS shown in Fig. 1 was selected for study, which has an overall *trans* geometry and an antiperiplanar relationship of each nitrogen lone pair to the transferring hydride. The true first-order saddle point for proton transfer from the carbon atom of CH$_2$=NH to the carbon atom of HN=CH$^-$ possesses C_2 symmetry, has a C···H···C angle of 176° and a dihedral angle of ~80° between the C=N bonds. The second-order saddle point of C_{2h} symmetry considered here (Fig. 1) is only 1.3 kJ mol^{-1} higher in energy and has a second (isotopically insensitive) imaginary frequency of 29*i* cm^{-1} for internal rotation about the C···C axis, indicative of an extremely flat potential in this coordinate. The reaction-coordinate vibrational mode for both the first- and second-order saddle-point species comprises almost entirely of asymmetric C···H stretching. The planar C_{2h} TS structure was chosen for evaluation of the PDKIEs to facilitate analysis of the normal-mode contributions into in-plane and out-of-plane components. The TSs for the HT and PT reactions are very similar geometrically: the principle difference is the shorter C···C distance for HT (2.68 Å) than for PT (2.91 Å), as predicted by qualitative MO theory.[6,8]

The HF/3-21G calculated semiclassical PDKIEs for HT and for PT at 298 K are given in Table 1. The first point to note is that neither value is large, although the PDKIE for HT is indeed 25% smaller than that for PT. The overall isotope effect may be factorized into mass/moment-of-inertia (MMI), excitational (EXC) and zero-point energy (ZPE) components.[4] The product MMI × EXC is similar for both HT and PT. The major part of the difference between the isotope effects for HT and PT arises from the ZPE component, which may be further factorized into contributions from particular groups of normal modes of the isotopomeric reactants and TSs. A Westheimer treatment[1] for linear TSs such as these would consider only the CH stretching modes: these alone

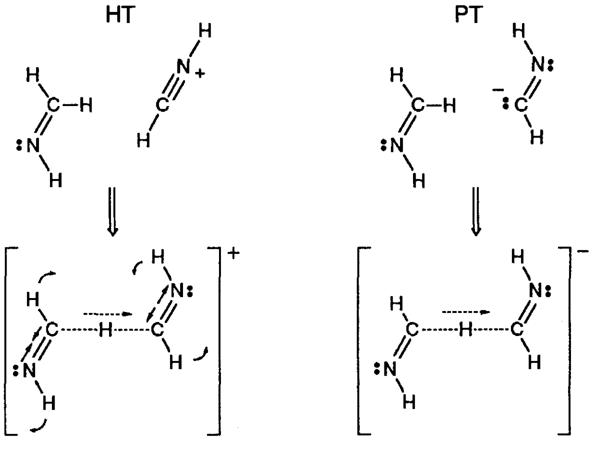

Fig. 1 Transition-state structures for analogous hydride-transfer (HT) and proton-transfer (PT) processes. Arrows indicate atomic motions in the reaction-coordinate vibrational modes.

Table 1 Analysis of semiclassical HF/3-21G primary kinetic deuterium isotope effects at 298 K for analogous hydride-transfer (HT) and proton-transfer (PT) reactions

	HT	PT
Overall $(k_H/k_D)_s$	3.30	4.38
MMI × EXC	1.20	1.26
ZPE	2.75	3.47
Factors contributing to ZPE:		
CH stretches	7.69	7.60
other in-plane modes	0.45	0.81
out-of-plane modes	0.80	0.56
$\nu^{\neq}_H/\nu^{\neq}_D$	1.15	1.39

give rise to isotope effects of the expected magnitude (~7) for both HT and PT: indeed that for HT is slightly the larger. The small overall isotope effects are due to compensation by isotopically sensitive vibrational modes other than CH stretching. It is instructive to consider in-plane and out-of-plane modes separately. A simple extension of the Westheimer treatment would include the C···H···C bending modes;[3] however, the in-plane C···H···C bend is particularly strongly coupled with other bending modes of each TS, so the whole group must be considered together. The out-of-plane C···H···C bend of the TS for PT is very isotopically sensitive and causes a very low ZPE factor (0.56) which reduces the overall PDKIE from ~7.6 to only 4.38. This confirms the suggestion[6] that, despite having longer C···H bonds, the TS for PT has stronger bonding and higher bending force constants than the TS for HT. The energies of the TSs, relative to the isolated reactants, are 100 and -19 kJ mol^{-1}, respectively for HT and PT, and the in-plane and out-of-plane C···H···C bending force constants are 0.05 and 0.14 md Å^{-1} for HT as against 0.28 and 0.33 md Å^{-1} for PT. For HT, the out-of-plane modes do contribute an inverse ZPE factor of 0.80, but the major inverse factor (0.45) is due to the in-plane bending and stretching modes. Inspection of the reaction-coordinate vibrational mode for HT reveals substantial participation of motion of all the other atoms besides the transferring hydrogen (see arrows in Fig. 1). This is to be expected, since the linear hydride acceptor species $HC{\equiv}NH^+$ must undergo substantial distortion in order to achieve its bent geometry in the TS. In contrast, the bent proton acceptor species $HN{=}CH^-$ is distorted only minimally in going to the TS for PT. This coupling of heavy-atom motion with hydrogen motion in the reaction coordinate is manifest in the ratio of isotopic reaction-coordinate frequencies, $\nu^{\neq}_H/\nu^{\neq}_D = 1.15$ for HT, which is appreciably different from the value of $(2)^{\frac{1}{2}} \approx 1.4$ which would obtain if this ratio were due solely to the mass difference of the transferring hydrogen;[4] the corresponding ratio for PT is 1.39.

In summary, the low semiclassical PDKIEs are not due to either (*i*) unsymmetrical or (*ii*) non-linear TS structures, since we have deliberately chosen linear, symmetrical TSs. The low isotope effect for PT arises from (*iii*) the influence of isotopically sensitive bending vibrations in the TS. The even lower isotope effect for HT is due to extensive participation in the reaction coordinate of degrees of freedom other than asymmetric C···H stretching.

We thank the SERC, the Nuffield Foundation and the Royal Society for support.

Received, 26th July 1991; Com. 1/03863J

References

1 F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.
2 M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, 1958, **80**, 4296; E. S. Lewis and M. C. R. Symons, *Q. Rev., Chem. Soc.*, 1958, **12**, 230.
3 R. A. More O'Ferrall, *J. Chem. Soc. B*, 1970, 785; *Proton-Transfer Reactions*, eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975.
4 L. Melander and W. H. Saunders, *Reaction Rates of Isotopic Molecules*, Wiley-Interscience, New York, 1980.
5 R. Stewart and T. W. Toone, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1243.
6 C. G. Swain, R. A. Wiles and R. F. W. Bader, *J. Am. Chem. Soc.*, 1961, **83**, 1945.
7 A. E. Pain and I. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1988, 1367.
8 I. H. Williams, A. B. Miller and G. M. Maggiora, *J. Am. Chem. Soc.*, 1990, **112**, 530.