SHORT COMMUNICATIONS

THE DEPENDENCE OF KINETIC ISOTOPE EFFECTS ON THE FREE ENERGY CHANGE FOR PROTON TRANSFER REACTIONS

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Recent interest in the use of kinetic isotope effects for determination of the mechanism of proton transfer reactions has led to discussion on the role played by three factors,[1–10] namely, the bending modes of the activated state, the "symmetric" stretching mode of the activated state and proton tunnelling (or, the asymmetric stretching mode of the activated state). It has been shown by Bell[1] that, under certain conditions, the contributions of proton tunnelling and of the "symmetric" stretching mode may cancel, which thus implicates the bending mode as the controlling factor in kinetic isotope effects.

The present communication aims to show that this alleged cancellation does not have general validity, and that it occurs only under a special set of circumstances. The basis for this claim lies in the fact that both factors are dependent upon the electrochemical free energy change of the proton transfer step and that, whilst the sign of the dependence is identical, one factor tends to increase the magnitude of the isotope effect whilst the other tends to decrease it.

The dependence of the degree of proton tunnelling, and the kinetic isotope effect, on the free energy of reaction has been theoretically and experimentally demonstrated by Bockris and Matthews[11] for the hydrogen evolution reaction at a mercury electrode. The same authors have also briefly demonstrated[12] the theoretical possibility of the dependence of the "symmetric" stretching mode on the free energy of reaction. They show that for proton tunnelling the correction to the kinetic isotope effect is unity for large positive free energies of reaction, ΔG_0, increases with decrease in ΔG_0, going through a maximum at $\Delta G_0 = 0$, and decreases towards

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unity for large negative values of ΔG_0. For example, in Figure 8 of ref.[11], for $A_0 = 0{\cdot}8\times10^{-12}$ erg, the value of η at $\Gamma = \Gamma_{max}$ is $-0{\cdot}8\times10^{-12}$ erg, and again, for $A_0 = 0$, $\eta(\Gamma = \Gamma_{max})$ is zero. Since

$$\Delta\bar{G}_0 = \Delta\bar{G}_0(\eta = 0)+\eta$$

or

$$A = A_0+\eta$$

in the terminology of ref.[11], then $\Delta\bar{G}_0(\Gamma = \Gamma_{max})$ is equal to zero. The tunnelling correction tends to unity at the extreme values of ΔG_0 since in one case the barrier height is zero, and in the other case the barrier width, for energy levels below the barrier maximum, is infinite.

Allowance for the "symmetric" stretching mode has a somewhat different effect owing to the fact that it contributes an additional term to the zero-point energy of the activated state, which term is larger for the lighter isotope. The result is a *decrease* of the isotope effect when this factor is allowed for. Proton tunnelling on the other hand leads to increased isotope effects. At large positive values of ΔG_0 the symmetric stretching correction is a maximum, and as ΔG_0 tends to zero the correction factor tends to unity. For $\Delta G_0 = 0$, the "symmetric" stretching frequency is zero (the mode is now truly symmetric) and the correction factor is unity. As ΔG_0 becomes more negative the correction factor becomes larger.

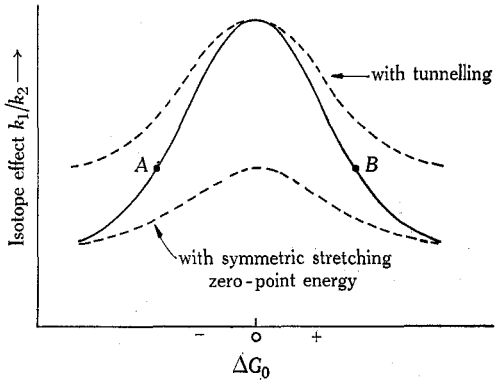

Fig. 1.—The dependence of the kinetic isotope effect for proton transfer on the free energy of reaction.

We thus have qualitatively the situation represented by Figure 1. From the figure it is seen that the two contributions cancel only at A and B. For all other values of ΔG_0, cancellation is not predicted.

Furthermore, the dependence of the isotope effect on ΔG_0 is enhanced by *both* contributions.

The dependence of the activated state bending frequency on ΔG_0 has also been tentatively explored by Matthews.[13] The contribution is such that it produces a minimum in the plot of k_1/k_2 against ΔG_0, due to the zero-point energy for the bending mode of the three-centre activated state A···H···B tending to a maximum as ΔG_0 tends to zero. Thus, some cancellation with the other two contributions is likely, and a reduction of the dependence of k_1/k_2 on ΔG_0 occurs.

[13] Matthews, D. B., Ph.D Thesis, University of Pennsylvania, Philadelphia, 1965.