CORRELATION OF KINETIC ISOTOPE EFFECTS WITH CHEMICAL BONDING IN THREE-CENTRE REACTIONS†

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INTRODUCTION

As a first orientation or zero order approximation to primary kinetic isotope effects it is useful to describe the isotope effect in terms of the zero point energy differences of the isotopic reactant molecules. This over-simplified picture gives qualitative answers for normal isotope effects. Significantly, it ignores the entire chemistry and structure of the transition state. It is just this problem, which is one of the central problems in chemical kinetics, about which one would like to get some information through the study of kinetic isotope effects. If isotope effects are to be useful for this purpose, it then becomes necessary to consider more refined models and calculations.

The formal theory of kinetic isotope effects within the framework of transition state theory has already been developed[1]. Although the full formal theory is one of simplicity, it is useful to consider various simplifications and approximations, which may be applicable to the particular problem at hand. The present paper is concerned with atom transfer or abstraction reactions of the type

$$A + BC \rightarrow AB + C \tag{1}$$
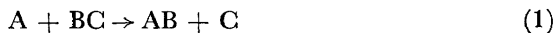
If B is a proton or hydrogen atom and if we are interested in kinetic isotope effects obtained by substitution of deuterium or tritium at B, then the model reaction given by equation (1) is a good approximation to the chemical reaction. This is a consequence of the fact that with respect to hydrogen all other chemical species have essentially infinite mass. Thus, there is little coupling between the motions of B and the once removed atoms that make up A or C. If A and/or C are hydrogen, then there are no atoms once removed to couple the motion. It is clear that the model reaction given by (1) neglects the coupling of B with atoms in C by bending vibrations. Thus, this model for the study of isotope effects is limited to the motion along the nuclear axis. In general, this is the most important contribution to the isotope effects, since bending force constants are generally one tenth those of

stretching force constants. This limitation of the present model calculation must be kept clearly in mind.

ISOTOPE EFFECT AND INTERATOMIC FORCES

Our purpose is to correlate the kinetic isotope effect with the chemical bonding of the isotopic atom both in the substrates A and BC and in the transition state. This is most conveniently done by writing the isotope rate equation (II. 20)†

$$k_1/k_2 = (\nu_1/\nu_2)_L{}^{\ddagger}\, f/f^{\ddagger} \tag{2}$$

in the $\bar{\gamma}$ approximation

$$\ln k_1/k_2 = \ln (\nu_1{}^{\ddagger}/\nu_2{}^{\ddagger})_L + \frac{\bar{\gamma}}{24}\left(\frac{\hbar}{kT}\right)^2 \sum_i \left(\frac{1}{m_{1i}} - \frac{1}{m_{2i}}\right)(a_{ii} - a_{ii}{}^{\ddagger}) \tag{3}$$

Equation (3) is in essence (II. 30), but removes some of the approximations in the latter. For simplicity we omit the symmetry number factor from equation (3). The $\bar{\gamma}$ method is an adaptation of the results of systems with not too large quantum effects or small changes in large quantum effects§. In the last section we shall give the results of our structural analysis in terms of equation (1). Such an analysis has, in part, also been given by Westheimer[4]. The conclusions are similar to those which one obtains more simply and directly by the $\bar{\gamma}$ method.

To calculate the kinetic isotope effect by the $\bar{\gamma}$ method we must know $(\nu_1{}^{\ddagger}/\nu_2{}^{\ddagger})_L$, the ratio of the frequencies of crossing the barrier (the imaginary frequencies) for the isotopic systems; *we must know the sine qua non, the change in the force constant of the isotopic atom between substrate and transition state*; finally an estimate must be made of $\bar{\gamma}$. The force constants of normal bond stretches are fairly well known from the literature of molecular spectroscopy. Force constants are to a good approximation transferable from one molecule to another. We can assume a_{ii} to be known in principle. We shall now develop a method to relate $a_{ii}{}^{\ddagger}$ with the structure of the transition state.

Since we neglect bending vibrations in the reactants, we will be consistent and neglect them in the transition state¶. This suggests that we treat the system

$$\begin{array}{ccc} & r_{AB} & r_{BC} \\ A & \text{---} \ B \ \text{---} & C \\ & \longleftarrow \ r_{AC} \ \longrightarrow & \end{array}$$
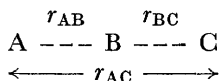
in the linear approximation. Associated with the displacements δr_{AB},

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† Throughout this paper we shall use the notation of Bigeleisen and Wolfsberg without further definition and shall refer to equations derived by them by equation number, *e.g.* (II.20) is equation (II.20) on page 23 of reference (1).

§ The expansion given recently by Bigeleisen and Goldstein[2] for the zero point difference of a pair of isotopic molecules extends the validity of the $\bar{\gamma}$ method. Further discussion of the validity of this powerful method is given in the paper by Wolfsberg and Stern at this Symposium.[3].

¶ It has been shown by Bell[5], that the motion of a proton between two fixed centres subject to a simple Coulomb force leads to the result that the tunnel effect exactly cancels the contribution of the bending vibration, provided these can be described in the first quantum approximation. Thus the introduction of these corrections in a real system will introduce minor modifications to the present argument.

δr_{BC}, and δr_{AC} are the force constants f_{AB}, f_{BC}, and f_{AC}. The most general harmonic potential for the transition state is

$$2V = f_{AB}\,\delta r_{AB}^2 + f_{BC}\,\delta r_{BC}^2 + f_{AC}\,\delta r_{AC}^2 \qquad (4)$$

We choose Z as the internuclear axis and δr_{ij} is $(Z_i - Z_j)$, the deviation of r_{ij} from its equilibrium value. Equation (4) is then

$$2V = f_{AB}(Z_A - Z_B)^2 + f_{BC}(Z_B - Z_C)^2 + f_{AC}(Z_A - Z_C)^2 \qquad (5)$$

which can be written

$$2V = f_{AB}(Z_A - Z_B)^2 + f_{BC}(Z_B - Z_C)^2 + f_{AC}(Z_A - Z_B + Z_B - Z_C)^2 \qquad (6)$$

Expansion of $(Z_A - Z_B + Z_B - Z_C)^2$ in equation (6) gives

$$2V = (f_{AB} + f_{AC})\,(Z_A - Z_B)^2 + (f_{BC} + f_{AC})\,(Z_B - Z_C)^2 + \\ + 2f_{AC}(Z_A - Z_B)\,(Z_B - Z_C) \qquad (7)$$

which is the form customarily found in the literature. If we designate r_{AB} as r_1 and r_{BC} as r_2, the correlation with the conventional notation is

$$f_{AB} + f_{AC} = f_1 \qquad (8)$$

$$f_{BC} + f_{AC} = f_2 \qquad (9)$$

$$f_{AC} = f_{12} \qquad (10)$$

Solution of Lagrange's equations for the motion of the three atom system ABC with the potential energy given by (5) leads to

$$\lambda_r + \lambda_L = (\mu_A + \mu_B)f_{AB} + (\mu_B + \mu_C)f_{BC} + (\mu_A + \mu_C)f_{AC} \qquad (11)$$

$$\lambda_r \lambda_L = M\mu_A \mu_B \mu_C(f_{AB}f_{BC} + f_{BC}f_{AC} + f_{AB}f_{AC}) \qquad (12)$$

where $\lambda = 4\pi^2 \nu^2$, ν is the vibrational frequency, $\mu_i = 1/m_i$ and M is the molecular weight of ABC. The square of the real stretching vibration is designated as λ_r; the motion across the barrier is described by λ_L.

The transition state differs from a stable molecule in that $\lambda_L \leqslant 0$. From equation (12) we arrive at the condition

$$f_{AB}f_{BC} + f_{BC}f_{AC} + f_{AB}f_{AC} \leqslant 0 \qquad (13)$$

At least one of the force constants must be negative, or two of them are zero. It is immediately apparent that transition states close to reactant will have f_{BC} positive and either f_{AB} or f_{AC} or both will be negative. For transition states close to product the converse will hold†. The Cartesian

† This result was obtained some thiry years ago by Eyring and Polanyi through semi-empirical quantum mechanical calculation of potential energy surfaces. Their surfaces have the restrictive peculiarity that $f_{AC} \sim 0$.

force constant along the internuclear axis for the i'th atom in the transition state is

$$a_{ii}^{\ddagger} = (\delta^2 V / \delta Z_i^2)_{Z_j, Z_k} \tag{14}$$

$$a_A^{\ddagger} = f_{AB} + f_{AC} \tag{15}$$

$$a_B^{\ddagger} = f_{AB} + f_{BC} \tag{16}$$

$$a_C^{\ddagger} = f_{BC} + f_{AC} \tag{17}$$

It now remains to correlate f_{AB}, f_{BC}, and f_{AC} with the structure of the transition state. For this purpose we shall adopt the simplification that the barrier is flat near the top[6, 7].

SYMMETRICAL TRANSITION STATES

Since the masses of all elements are essentially infinite with respect to the proton mass, a symmetrical transition state for the case B=H implies $f_{AB} = f_{BC}$. Thus, the symmetric flat top barrier is one for which

$$f_{AB}^2 + 2f_{AB}f_{AC} = 0 \tag{18}$$

or

$$f_{AB} = 0; \quad -2f_{AC} \tag{19}$$

From equations (15–17) we find that the solution $f_{AB} = -2f_{AC}$ leads to a state which is unstable with respect to the displacement of each of the atoms A, B, and C. This is not the transition state. The solution $f_{AB} = 0 = f_{BC}$ describes the transition state. Atoms A and C are bound, but B moves in a force free field between A and C. For such an atom the reduced partition functions ratio s/s' f is unity. A reaction which proceeds through such a transition state from a given specified reactant will show the maximum isotope effect. This is true both for the energy and frequency factors of equation (3).

The ratio $(\nu_1^{\ddagger}/\nu_2^{\ddagger})_L$, although indeterminate, 0/0, is finite. We evaluate it as follows. From equation (11) we have for the case $f_{AB} = f_{BC} = 0$

$$\lambda_r = (\mu_A + \mu_C) f_{AC} \tag{20}$$

The real stretching vibration involves the motion of A and C. B stands still in this normal vibration; the frequency of this vibration is independent of the mass of B. From equation (12)

$$(\nu_1^{\ddagger}/\nu_2^{\ddagger})_L = \left(\frac{M_1^{\ddagger} m_{2B}}{M_2^{\ddagger} m_{1B}}\right)^{1/2} \tag{21}$$

and

$$\ln (k_1/k_2) = \tfrac{1}{2} \ln \left(\frac{M_1^{\ddagger} m_{2B}}{M_2^{\ddagger} m_{1B}}\right) + \frac{\bar{\gamma}}{24} \left(\frac{\hbar}{kT}\right)^2 \left(\frac{1}{m_{1B}} - \frac{1}{m_{2B}}\right) (a_B) \tag{22}$$

ASYMMETRIC TRANSITION STATES

We have shown that the symmetric transition state leads to the maximum isotope effect for atom transfer reactions. We shall now consider the isotope effects for such reactions in which the transition state is close to reactant and product respectively.

When the transition state is close to reactant $f_{BC} \gg f_{AB}$. Thus, $a_B{}^{\ddagger}$ is f_{BC} and the bonding on B has not changed appreciably from that in the reactant, BC. The isotope effect is small and depends upon the amount the B–C bond is weakened (strengthened) between reactant and transition state.

$$\ln k_1/k_2 \simeq \ln (\nu_1{}^{\ddagger}/\nu_2{}^{\ddagger})_L + \frac{\bar{\gamma}}{24} \left(\frac{\hbar}{kT}\right)^2 \left(\frac{1}{m_{1B}} - \frac{1}{m_{2B}}\right)(a_B - f_{BC}) \quad (23)$$

The $(\nu_1{}^{\ddagger}/\nu_2{}^{\ddagger})_L$ consistent with the assumption that $f_{BC} \gg f_{AC}$ is found as follows:

$$\lambda_r = (\mu_B + \mu_C)f_{BC} + (\mu_A + \mu_C)f_{AC} \quad (24)$$

$$(\nu_1{}^{\ddagger}/\nu_2{}^{\ddagger})_L = \left(\frac{M_1{}^{\ddagger} m_{2B}}{M_2{}^{\ddagger} m_{1B}}\right)^{1/2} \left(\frac{\lambda_{2r}}{\lambda_{1r}}\right)^{1/2} \quad (25)$$

$$= \left(\frac{M_1{}^{\ddagger} m_{2B}}{M_2{}^{\ddagger} m_{1B}}\right)^{1/2} \left(\frac{(\mu_{2B} + \mu_C)f_{BC} + (\mu_A + \mu_C)f_{AC}}{(\mu_{1B} + \mu_C)f_{BC} + (\mu_A + \mu_C)f_{AC}}\right)^{1/2} \quad (26)$$

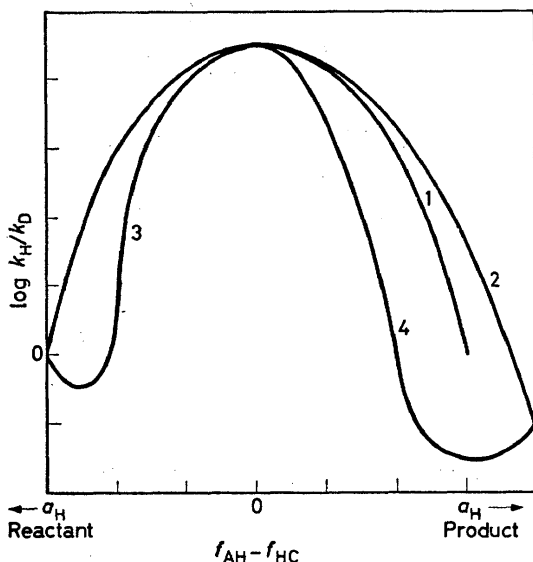We note $(\nu_1{}^{\ddagger}/\nu_{2L}{}^{\ddagger})$ lies in the range $1 \to \sqrt{2}$.

Figure 1. Log k_H/k_D (schematic) as a function of the structure of the transition state for proton or hydrogen atom transfer reactions

1: $(a_B)_{\text{reactant}} = (a_B)_{\text{product}}$
2: $(a_B)_{\text{product}} > (a_B)_{\text{reactant}}$
3: $(f_{AB} + f_{BC}) > (a_B)_{\text{reactant}}$
4: $(f_{AB} + f_{BC}) > (a_B)_{\text{product}} > (a_B)_{\text{reactant}}$

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The treatment of reactions for transition states close to the product follows in an analogous manner. The appropriate relationships are

$$\ln (k_1/k_2) = \ln (\nu_1^\ddagger/\nu_2^\ddagger)_L + \frac{\bar{\gamma}}{24} \left(\frac{\hbar}{kT}\right)^2 \left(\frac{1}{m_{1B}} - \frac{1}{m_{2B}}\right) (a_B - f_{AB}) \quad (27)$$

$$(\nu_1^\ddagger/\nu_2^\ddagger)_L = \left(\frac{M_1^\ddagger m_{aB}}{M_2^\ddagger m_{1B}}\right)^{1/2} \left(\frac{(\mu_A + \mu_{2B})f_{AB} + (\mu_A + \mu_C)f_{AC}}{(\mu_A + \mu_{1B})f_{AB} + (\mu_A + \mu_C)f_{AC}}\right)^{1/2} \quad (28)$$

If the product has a very strong force constant, f_{AB}, compared to reactant. a_B, and the transition state is close to the product, then inverse isotope effects may occur. The frequency factor ratio is again in the range $1 \to \sqrt{2}$. Inverse isotope effects do not, however, speak unequivocally for transition states close to the product. We can see that small inverse isotope effects can occur for transition states close to the reactant if $f_{AB} + f_{BC} > a_B$ and if the temperature-dependent term outweighs the temperature-independent term. Symmetric transition states are accompanied only by normal, positive isotope effects. A summary of a number of different possibilities is shown in *Figure 1*.

EXACT EQUATIONS

In this section we give the exact equations for the models discussed. The reduced partition function ratios s/s' f and s/s' f‡ are respectively

$$s/s' f = \prod^{3n-6} \frac{\nu_i}{\nu_i'} e^{\Delta u_i^\ddagger/2} \frac{(1 - e^{-u_i'})}{(1 - e^{-u_i})} \quad (29)$$

$$s/s' f^\ddagger = \prod^{3n-7} \frac{\nu_i^\ddagger}{\nu_i'^\ddagger} e^{\Delta u_i^\ddagger/2} \frac{(1 - e^{-u_i'^\ddagger})}{(1 - e^{-u_i^\ddagger})} \quad (30)$$

For a linear molecule in which we neglect the bending vibrations, the product in the reactant runs over the $n - 1$ stretching vibrations along the internuclear axis. For the transition state the product is over the $n - 2$ real stretching vibrations. From the product rule for this symmetry class we have

$$\prod^{n-1} \frac{\nu_1 \ldots \nu_i \ldots \nu_{n-1}}{\nu_1' \ldots \nu_i' \ldots \nu_{n'-1}} = \prod_\alpha \left(\frac{M}{M'} \frac{m_\alpha'}{m_\alpha}\right)^{1/2} \quad (31)$$

The number of isotopic substitutions is designated by the subscript α. Inasmuch as the isotope rate equation (2) has $(\nu_1^\ddagger/\nu_2^\ddagger)_L$ multiplying the reduced partition function ratio, this factor, $(\nu_1^\ddagger/\nu_2^\ddagger)_L$, can be combined with the $n - 2$ frequency ratios in $f^\ddagger$ to give the product rule ratio along the internuclear axis. We then obtain the interesting result

$$\ln (k_1/k_2) = 1/2 \ln \left(\frac{M_2 M_1^\ddagger}{M_1 M_2^\ddagger}\right) + 1/2 \left(\sum^{n-1} \Delta u_i - \sum^{n-2} \Delta u_i^\ddagger\right) +$$

$$+ \sum^{n-1} \ln \frac{(1 - e^{-u_i'})}{(1 - e^{-u_i})} - \sum^{n-2} \ln \frac{(1 - e^{-u_i'^\ddagger})}{(1 - e^{-u_i^\ddagger})} \quad (32)$$

The so-called "pre-exponential or temperature-independent factor" is the ratio of the square roots of the molecular weights of the reactants and transition states. This is exactly the same result as that of the equilibrium isotope effect and is based on the density of states in momentum space[8]. It is identically the result which obtains from the collision theory. Thus, one realizes from this general derivation that, other statements to the contrary[9], there is no distinction between the transition state theory and the collision theory on this question.

The zero point energy difference in the real vibration, both in the reactant and transition state, is obtained by putting λ_L equal to zero in equation (11). We thus see that apart from numerical factors, the zero point energy difference in equation (32) is quite analogous to the force constant shift in equation (3). The masses of the atoms A and B become of significance in determining the details of the isotope shift on the molecular vibration and zero point energy. The Boltzmann excitation terms are opposite in direction from the temperature-independent term. At high temperatures, the $(M_2/M_1)^{1/2}$ ratio is exactly cancelled by the Boltzmann excitation terms. For the transition state everything in $(M_2^\ddagger/M_1^\ddagger)$ is cancelled except the contribution of $\nu_{1L}^\ddagger/\nu_{2L}^\ddagger$, and thus the high temperature limit for the temperature independent factor becomes $\nu_{1L}^\ddagger/\nu_{2L}^\ddagger$. This old result[8, 10, 11] brings some recent discoveries [12] on this subject into question.

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