Reply to ``Comment on the Calculation of Temperature-Independent Factor in Isotopic Rate-Constant Ratios"

Carole R. Gatz

In usual transition-state theory, the normal-coordinate set Q (of which the properly normalized reaction coordinate Q_1 is a member) is connected to the mass-weighted Cartesian displacement coordinates by an orthogonal transformation and one consequently can deduce from an equation of the form of Eq. (2), Ref. 1, how the various atoms move during Q_1 motion. In the Gatz treatment, the Gatz coordinate set Q is connected to the *internal* displacement coordinates by an orthogonal transformation,[13] and one can, therefore, again deduce the atomic motions from the equation for Q_1. It is important to note that a given expression for the reaction coordinate in terms of internal displacement coordinates [as in Eq. (2), Ref. 1] may not refer to the same type of motion in usual transition-state theory and in the Gatz treatment. Thus, in the Gatz treatment, the case where the reaction coordinate is taken to be a simple stretching coordinate corresponds to reaction motion in which the relevant bond is elongating or shortening without affecting the other internal displacement coordinates, while in the usual transition-state treatment,[6,8] this (normal-mode) reaction coordinate corresponds to reaction motion in which only the two atoms connected by the stretching coordinate are moving.

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[2] H. S. Johnston, W. A. Bonner, and D. J. Wilson, J. Chem. Phys. **26**, 1002 (1957).
[3] M. J. Stern and M. Wolfsberg, J. Chem. Phys. **39**, 2776 (1963).
[4] M. Wolfsberg and M. J. Stern, Pure Appl. Chem. **8**, 225 (1964).
[5] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941).
[6] M. Wolfsberg, J. Chem. Phys. **33**, 21 (1960).
[7] N. B. Slater, in his *Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, N.Y., 1959), which summarizes most of his earlier work on rates, has been able to formulate a classical "transition-state-type" theory in which the reaction coordinate need not be a normal coordinate. Although the rate-constant equation which he obtains has the same form as that obtained in usual transition-state theory, it is not equivalent since the $3N$-7 real frequencies of the transition state in Slater's formulation are not (except coincidentally) normal-mode frequencies of the whole transition-state system. Slater uses the separability of the reaction coordinate as an extra assumption in his original quantum-mechanical formulation and obtains then, by proceeding in a manner similar to that of usual transition-state theory, a rate-constant equation of the same form as that of usual transition-state theory but not equivalent to it. It is of interest that in a more recent paper, Slater [J. Chem. Phys. **35**, 445 (1961)] concludes (although for completely different reasons than ours) that the reaction coordinate in his theory should be a normal coordinate. To our knowledge, no one has derived the usual form of the quantum rate-constant equation without imposing separability of the reaction coordinate. In the original Slater method as used by Gatz, the expression for the reaction coordinate Q_1 in terms of the internal displacement coordinates q_i is obtained from an inspection of the potential-energy surface with the (*ad hoc*) proviso that the transformation $Q = Aq$ be orthogonal. This isotope-independent coordinate is then made "separable" by arbitrarily dropping cross terms in the kinetic-energy expression. Some of these cross terms may even depend on the mass of the isotopically substituted atom.

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[9] J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. **21**, 1972 (1953); **22**, 1264 (1954).
[10] P. E. Yankwich and R. M. Ikeda, J. Am. Chem. Soc. **81**, 1532 (1959).
[11] See our comments on this nomenclature in Ref. 4.
[12] Calculations of this type in effect yield first-order perturbation-theory approximations to $\nu_x^{\ddagger\prime}/\nu_x^{\ddagger}$ [E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955), p. 189].
[13] See Footnote 7. While Slater has pointed out that an orthogonal transformation of internal displacement coordinates can be used to put the transition-state potential-energy expression into the form he desires (N. B. Slater, *Theory of Unimolecular Reactions*, p. 107), it is not necessary to use an orthogonal transformation for this purpose and this *ad hoc* imposition of orthogonality is not usually considered an essential part of his theory.

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IN usual transition-state theory the reaction coordinate is assumed to be that normal coordinate of the activated complex which corresponds to an imaginary frequency. Since energies in normal modes are separable, the reaction rate is readily formulated as the rate at which systems pass through a surface orthogonal to the (normal) reaction coordinate at the activation point. The normal mode assumption thus plays an essential part in the usual formulation; it is nevertheless an assumption.

In the isotope-effect calculations reported[1] recently, the reaction coordinate was assumed to be a particular direction in the potential-energy surface, such as the direction of steepest descent from the activation point, and not necessarily a normal coordinate. This reaction coordinate can be written as a linear combination of internal (not mass-weighted) displacement coordinates q_i

$$Q_i = \sum_i^{3N-6} a_{1i} q_i. \tag{1}$$

The coefficients a_{1i} are independent of isotopic substitution to the extent that the potential-energy surface, neglecting zero-point energies, is independent of isotopic substitution. It has been pointed out by Stern and Wolfsberg[2] that if a normal coordinate is written in the form of Eq. (1), the coefficients will be isotope dependent, except in certain special cases. Therefore the reaction coordinate of Eq. (1) is not a generalization of the usual normal-mode assumption. On the other hand, it should not be considered an approximation to the normal-mode treatment. The

two cases represent two different assumptions as to the nature of the reaction coordinate.

In abandoning normal reaction coordinates, one also loses the convenient separability of energy. However, following Slater,[3] one can assume[4] that the distribution of energy in coordinates orthogonal to the reaction coordinate, averaged over many systems at the instant they pass through the activation surface, is equal to the distribution of energy of one system constrained to remain in the activation surface, averaged over time. The reaction rate can then be formulated in the usual fashion, and one obtains for the rate-constant ratio in an intramolecular isotope effect[5]

$$\frac{k'}{k} = \left(\frac{A^{\ddagger'}B^{\ddagger'}C^{\ddagger'}}{A^{\ddagger}B^{\ddagger}C^{\ddagger}}\right)^{\frac{1}{2}} \prod_{j}^{3N-7} \frac{\sinh(u_j^{\ddagger}/2)}{\sinh(u_j^{\ddagger'}/2)}. \quad (2)$$

Primed and unprimed quantities refer to two isotopic species; $A^{\ddagger}$, $B^{\ddagger}$, $C^{\ddagger}$ are the three principal moments of inertia of the activated complex; and $u_j = h\nu_j/kT$, where ν_j is one of the $3N-7$ Slater-type frequencies of the constrained system and is not, in general, one of the normal frequencies of the unconstrained system.

The usual form of the Redlich–Teller product rule (in terms of the $3N-6$ normal frequencies of an unconstrained activated complex) can be applied to Eq. (2) to give

$$\frac{k'}{k} = \prod_{i}^{3N-6} \frac{u_i^{\ddagger'}}{u_i^{\ddagger}} \prod_{j}^{3N-7} \frac{\sinh(u_j^{\ddagger}/2)}{\sinh(u_j^{\ddagger'}/2)}, \quad (3)$$

which can be written in the form

$$\frac{k'}{k} = \left(\prod_{i}^{3N-6} \frac{u_i^{\ddagger'}}{u_i^{\ddagger}} \prod_{j}^{3N-7} \frac{u_j^{\ddagger}}{u_j^{\ddagger'}}\right)\left[\prod_{j}^{3N-7} \frac{u_j^{\ddagger'}}{u_j^{\ddagger}} \frac{\sinh(u_j^{\ddagger}/2)}{\sinh(u_j^{\ddagger'}/2)}\right]. \quad (4)$$

The first quantity in parentheses is the temperature-independent factor TIF.

The above discussion is intended to clarify the distinction between frequencies of unconstrained and constrained systems, denoted by Subscripts i and j, respectively. The following discussion is intended to clarify the method of calculating them.

If $\mathbf{A}$ is a real, unitary[6] transformation matrix such that $\mathbf{Aq}=\mathbf{Q}$ with Q_1 the reaction coordinate, then $\mathbf{F}^*=\mathbf{AFA}^{-1}=\mathbf{AFA}^{\dagger}$ (transpose) and $\mathbf{G}^*=\mathbf{AGA}^{\dagger}$. The $3N-7$ constrained frequencies ν_j are obtained from the roots of the reduced secular equation

$$|\, \mathbf{F}^*_{11} - [(\mathbf{G}^*)^{-1}]_{11}\lambda \,| = 0,$$

where the subscript 11 indicates deletion of the first row and column. This deletion results from the artificial constraints $Q_1=0$ and $\dot{Q}_1=0$ and does not require that any elements of $\mathbf{F}^*$ or $\mathbf{G}^{*-1}$ be zero or independent of isotopic substitution.

The characteristic equations for the constrained and unconstrained systems are, respectively,

$$\prod_{j}^{3N-7} \lambda_j = |\, \mathbf{F}_{11}^*\{[(\mathbf{G}^*)^{-1}]_{11}\}^{-1} \,|$$

and

$$\prod_{i}^{3N-6} \lambda_i = |\, \mathbf{F}^*\mathbf{G}^* \,|.$$

Since $\mathbf{F}^*$ is very nearly independent of isotopic substitution and $\lambda = 4\pi^2\nu^2$, TIF in Eq. (4) becomes

TIF $= \{|\, G'^* \,||\, [(G'^*)^{-1}]_{11} \,|/|\, G^* \,||\, [(G^*)^{-1}]_{11} \,|\}^{\frac{1}{2}}.$ (5)

This is the general equation used for calculations of TIF in Ref. 1.

[1] C. R. Gatz, J. Chem. Phys. **44**, 1861 (1966).
[2] M. J. Stern and M. Wolfsberg, J. Chem. Phys. **46**, 823 (1967), preceding paper.
[3] N. B. Slater, Proc. Leeds Phil. Lit. Soc. Sci. Sect. **5**, 75 (1949); *Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, N.Y., 1959). Although Slater's treatment is usually applied to reactant structures (with energies in excess of the activation energy) in this case it is applied to transition-state structures.
[4] This assumption could perhaps be included in the fundamental equilibrium assumption of the transition-state approach. As an explicit and independent assumption, it emphasizes the difference in the two formulations discussed here.
[5] This discussion is limited to intramolecular isotope effects in order to simplify the equations. The extension to intermolecular effects is straightforward.
[6] This is a sufficient but not necessary condition. In order to obtain the secular equation for the constrained system it is necessary to express $\mathbf{F}$ and $\mathbf{G}$ in terms of motion in the reaction coordinate and in coordinates orthogonal to it. The latter coordinates need not be orthogonal to each other, although they must be linearly independent. A unitary transformation, which completely preserves orthonormality, is convenient, for then $\mathbf{A}^{-1}=\mathbf{A}^{\dagger}$ and the equation for TIF reduces to the form on the right in Eq. (4), Ref. 1.

Errata

Erratum: Effect of Spin–Orbit Interactions on the Zero-Field Splitting of the NH Radical*

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IT was pointed out to us by Lefebvre-Brion[1] that the functions $^1\Psi_{xx}$ and $^1\Psi_{yy}$, which we defined in Eqs. (14) and (15), do not have the proper symmetry for representing the excited states of the NH radical.