Comment on the Calculation of ``Temperature-Independent Factor'' in Isotopic Rate-Constant Ratios

Marvin J. Stern and Max Wolfsberg

Reference 8 represents an indirect determination of τ_A. Radiative lifetime data of $N_2(1+)$ ($B\,^3\Pi \rightarrow A\,^3\Sigma$) also may be used to refine the lifetime and associated transition probability values for the VK system. This is possible via the ratio, by Carleton and Oldenberg[9] (C and O) of the radiative lifetimes of the A and B states: $\tau_A/\tau_B = (1.6\pm0.4)\times10^6$ where, for this experiment τ_A pertains to $v=0$ of the $A\,^3\Sigma$ state and τ_B refers to $v=1$ of the $B\,^3\Pi$ state. From this C and O deduced $\tau_A = 2$ sec, but this was based in part on $N_2(1+)$ data now known to be incorrect or treated inadequately.[2]

We measured $\tau_B = 8.1\pm1.1$ μsec directly. A pulsed rf discharge[10] produced the $N_2(1+)$ system strongly, and the lifetime was measured via well-known pulse-sampling techniques.[11] Our value agrees well with the independent measurement of 7.5 μsec by Jeunehomme.[12] These results are from extrapolation of pressure-dependent data to zero pressure, thus eliminating the effect of collisions. Thus, if we take $\tau_B = 7.9\pm0.5$ μsec and accept the C and O ratio, then $\tau_A = 12.6\pm4.3$ sec.

If the ratio from C and O is tenable, it appears that the lowest electronically excited state of N_2 has a mean radiative lifetime close to 13 sec rather than about 1 sec and the former is recommended for use, such as in interpretation of aeronomical spectral studies of the aurora. Our good agreement with Brennen's lower bound mentioned earlier supports this recommendation, and also the work of C and O. The agreement is particularly marked when the diversity of approaches and experiments is considered. Thus Nicholls' absolute transition probabilities[1] should be revised. However, our results do not invalidate the ratios given by Carleton and Papaliolios' data.[13]

Conversations with Professor N. P. Carleton of Harvard University on the above were helpful, as were the constructive criticisms of the referees, and all are gratefully acknowledged.

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Comments

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IN a recent paper[1] on isotopic rate-constant-ratio calculations in the quantum-mechanical transition-state formulation, Gatz states that "equating the reaction coordinate with a normal coordinate is a convenient but restrictive assumption" and cites several references[2-4] as examples where such a procedure has been followed. She then carries through a number of calculations in which the reaction coordinate is taken as an arbitrary linear combination of internal displacement coordinates.

Actually, equating the reaction coordinate with a normal coordinate should not be considered an extra assumption but an integral part of the quantum-mechanical formulation of usual transition-state theory.[5,6] Separability of the reaction coordinate (i.e., the absence of cross terms involving this coordinate in both the quadratic potential- and kinetic-energy expressions) requires, due to the dynamics of molecular motion, that it be a normal coordinate[7]; thus, for usual transition-state theory, the $3N-7$ real transition-state frequencies which appear in the theoretical expression for isotopic rate ratios [Eq. (1), Ref. 1] are the real normal-mode frequencies for the whole transition-state system and not those frequencies corresponding to Eq. (5), Ref. 1 (unless the coordinate which has been separated out is, indeed, a normal coordinate). The factor $\nu_x^{\ddagger\prime}/\nu_x^{\ddagger}$ in Eq. (1), Ref. 1, appears only because of the application of the Teller–Redlich product rule.[8] Since the $3N-7$ real transition-state frequencies must correspond to normal modes of the whole system, it follows that, in usual transition-state theory, the imaginary (or zero) frequency $\nu_x^{\ddagger}$ must also correspond to a normal mode.

Gatz' calculations, as well as previous general calculations of the same type,[9,10] must be considered as approximations to usual transition-state theory calculations of $\nu_x^{\ddagger\prime}/\nu_x^{\ddagger}$ (sometimes referred to as "temperature-independent factor"[11]), since the (normal-mode) reaction coordinate Q_1 expressed in terms of internal displacement coordinates, as in Eq. (2), Ref. 1 (*vide infra* for the meaning of Q_1), will not, except in some special cases, be isotope independent[9] [i.e., the a_{1i} coefficients in Eq. (2), Ref. 1, will generally depend on the isotopic substitution].[12]

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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[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** = A**q** 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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[12] Calculations of this type in effect yield first-order perturbation-theory approximations to $v_x^{\ddagger\prime}/v_x^{\ddagger}$ [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.

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

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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