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Golden Rule Treatment of Hydrogen-Transfer Reactions. 1. Principles[†]

Willem Siebrand,* Timothy A. Wildman,[‡] and Marek Z. Zgierski

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6. *Received November 9, 1983*

Abstract: Reactions involving tunneling of a hydrogen or deuterium atom through a potential energy barrier are described in terms of a formalism analogous to that used for radiationless transitions. The initial and final states of the transfer are taken to be vibrational eigenstates of the non-interacting reactants and products, respectively. In this formalism transfer occurs when the interaction is turned on; the rate of transfer is proportional to squared matrix elements of the interaction operator between the initial and final states. The barrier shape does not enter the description explicitly but may be obtained from the vibrational potentials determining the initial and final states and the interaction operator; these potentials can be derived from spectroscopic information. The transfer rate constants and barrier shapes, obtained as functions of the interaction operator, are compared with those derived according to the usual tunneling formalism in which the observed rate constants are interpreted in terms of an empirical barrier shape such as an Eckart barrier. These empirical shapes are found to be inconsistent with available spectroscopic information. On the other hand, one-dimensional barriers constructed on the basis of this information fail to account for the transfer data. This inconsistency can be removed by including low-frequency, non-hydrogenic modes into the formulation proposed: such a generalized model is shown to yield a satisfactory description of the temperature and isotope dependence of observed transfer rate constants. The low-frequency modes cause barrier oscillations which periodically create favorable transfer conditions, and they also assist in balancing the energy between reactants and products. Rate-constant expressions are derived which involve a high-frequency hydrogenic mode and a low-frequency non-hydrogenic mode, assumed adiabatically separable. The resulting rate constants, plotted as an exponential function of T rather than $1/T$, show a constant part at low temperatures followed by a quasilinear part, in qualitative agreement with observed behavior patterns. Such plots are studied as a function of the anharmonicity of the potentials and of the dependence of the interaction on the separation of the interacting partners.

Reactions involving hydrogen transfer differ from most other chemical reactions in that they behave nonclassically. The classical theory of chemical reactions is based on the concept of an activated complex, a configuration of maximum energy through which the reactants must pass before they can form products. In general, thermal energy is required to cross such a potential energy barrier, namely enough to get over the top. If the barrier height seen by the reactants is given by E_a and the reaction follows (pseudo-) first-order kinetics, the temperature dependence of the reaction rate constants can be expressed in the form of the familiar Arrhenius equation

$$k(T) = A \exp(-E_a/k_BT) \equiv A \exp(-\beta E_a) \qquad (1)$$

where k_B is the Boltzmann constant. To "derive" this equation, one notes that the fraction of the reactant molecules with enough thermal energy to form the activated complex is given by the Boltzmann factor $\exp(-\beta E_a)$. In this statistical "derivation", the "frequency factor" A is simply a constant. In more elaborate treatments, that do not ignore the dynamics of the reaction, A is usually temperature dependent, e.g., proportional to T^{-1} in Eyring's transition-state theory[1,2] or $T^{-1/2}$ in some other models[3,4] (see below). However, this temperature dependence is typically so much weaker than that introduced by the Boltzmann factor in eq 1 that it has little effect on the analysis of experimental data.

This picture of a chemical reaction as a barrier crossing is incomplete, however, unless we allow for the possibility of barrier penetration. Quantum mechanically, particles with a kinetic energy smaller than E_a can still cross the barrier by tunneling through it. This transfer mechanism depends critically on the wave character of the "particle": as a result, the rate of tunneling is very sensitive to the particle mass. Tunneling is only important for light particles such as electrons and protons; moreover the rate of tunneling will be isotope dependent, namely much faster for protons than for deuterons. The observation of a strong deuterium effect on the rate of a hydrogen-transfer reaction has long been taken as an indication that the transfer proceeds by tunneling.[5]

This quantum-mechanical tunneling is the subject of the present paper. The method used to describe such nonclassical transfer will, however, avoid the usual tunneling formalism. Instead of formulating the transfer in terms of barrier penetration, we shall describe it as a radiationless transition between potential energy surfaces. The basic approach has been introduced several years ago.[4] It is our purpose to show that this approach is simpler, both conceptually and practically, than the one in common use.

The tunnel effect in chemical reactions has been the subject of numerous papers, several reviews,[6-8] and at least one book.[5] Yet in many respects the concept remains ambiguous and controversial. Not only is it difficult to prove that a given reaction proceeds via tunneling, it is even difficult to define the term tunneling unambiguously. The hydrogen atoms themselves, one presumes, are unaware that they are tunneling: from their vantage point the barrier is, like beauty, only present in the eye of the observer. Moreover, not all observers will see the barrier but only those that have not yet overcome their classical prejudice. In other words, barriers are not observables in a quantum-mechanical sense: they are simply intermediate stages in the calculation.

The observables in chemical reactions are the rates of disappearance of reactants and appearance of products. If conditions are chosen such that these rates follow first-order kinetics, the reaction proceeds exponentially in time and can be expressed in terms of a (unimolecular) rate constant. In accord with the laws of quantum mechanics, exponential growth and decay rate constants can be expressed in a unique way through the "golden rule" of time-dependent perturbation theory.[9] The same rule applies to decay of optical emission due to radiative and nonradiative transitions. In all these cases the exponential decay rate constant is proportional to the square of the transition matrix element $\langle f|U|i\rangle$, where $|i\rangle$ and $|f\rangle$ are the initial and final states of the

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[†] Issued as NRCC No. 23386.

[‡] Research associate.

(1) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

(2) Glasstone, S.; Laidler, K. J.; Eyring, H. "The Theory of Rate Processes"; McGraw-Hill: New York, 1941.

(3) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860.

(4) Laplante, J.-P.; Siebrand, W. *Chem. Phys. Lett.* **1978**, *59*, 433.

(5) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: London, 1980, and references therein.

(6) Johnston, H. S. *Adv. Chem. Phys.* **1960**, *3*, 131.

(7) Caldin, E. G. *Chem. Rev.* **1969**, *69*, 135.

(8) Harmony, M. D. *Chem. Soc. Rev.* **1972**, *1*, 211.

(9) See, e.g.: Merzbacher, E. "Quantum Mechanics", 2nd ed.; Wiley: New York, 1970.

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unperturbed system and U is the interaction operator. For radiative transitions, $|i\rangle$ and $|f\rangle$ are molecular wave functions, and U is (in most cases) the electric dipole operator. Analogously, for chemical reactions, $|i\rangle$ is the wave function representing non-interacting reactants, $|f\rangle$ is that representing non-interacting products, and U is the interaction causing the reaction. In the case of hydrogen transfer, $|i\rangle$ and $|f\rangle$ will be vibrational wave functions describing the motion of the hydrogen atom in the non-interacting reactants and products, respectively, and U will be proportional to the overlap of electronic wave functions of the atoms between which the hydrogen is transferred. No barriers appear explicitly in this picture, which remains valid whether the transfer is classically allowed ("over the barrier") or forbidden ("through the barrier"), provided that the rate of transfer is small relative to the vibrational period. This restriction is not significant for transfer reactions accessible by conventional kinetic techniques.

Although we introduced the golden-rule approach to transfer via tunneling several years ago,[4] its advantages over the semiclassical tunneling approach[2] have not been generally recognized. In this series of papers, we present a much more complete description of our method and show by example how it can be applied to analyze observed rate constants and activation energies. These analyses make use of spectroscopic and/or quantum-chemical information to construct realistic potentials, so as to avoid the arbitrariness inherent in analytical barrier shapes adjusted empirically to fit observed rate constants. Following a brief earlier communication,[10] the present paper sketches the basic framework of the method in preparation for an application to specific hydrogen-transfer data in the following paper.[11]

1. Barriers

Experimental indicators that a given hydrogen-transfer reaction proceeds through tunneling are (i) a large primary deuterium isotope effect and (ii) a temperature dependence deviating strongly from that predicted by the Arrhenius equation (eq 1). It has been noted[12] that the rate constants of such reactions often appear to follow a rate law of the form

$$k(T) = k(0)\exp(CT) \tag{2}$$

In terms of the Arrhenius equation, this means that the effective activation energy, measured over a small range of temperatures, increases if this range is chosen at higher and higher temperatures. Qualitatively this agrees with the notion of tunneling through barriers which narrow toward the top: a higher temperature means a higher energy in the initial state and hence a shorter tunneling distance and a faster rate of transfer. More specifically, the observation of a rate law of the form of eq 2 and the value of the parameter $k(0)$ associated with it fixes the shape and height of the barrier within narrow limits. In many papers dealing with hydrogen tunneling,[5] the observed rates are interpreted in terms of such empirical barriers. Typically,[5,13] one adopts a convenient analytical form for the barrier shape and adjusts the parameters determining height and width until they yield an acceptable reproduction of the data. As we showed in the earlier note,[10] such barriers do not compare favorably with barriers derived from spectroscopic data. The latter can be constructed starting from the initial- and final-state configurations where the hydrogen atom will generally move in an approximately harmonic potential. The region where the initial- and final-state potentials cross will determine the height of the barrier; in principle, the interaction, leading to an avoided crossing, can be calculated quantum chemically. Putting such estimates together, one arrives at a barrier totally different from the barrier derived empirically from the transfer data.[10]

Hence we are faced with a dilemma: the barrier derived empirically from transfer data disagrees with known spectroscopic equilibrium properties, whereas the barrier derived from those properties yields unacceptable transfer rates. Moreover, these two barriers are far too different to permit a compromise that would reproduce both transfer and spectroscopic data. Clearly, conventional one-dimensional barrier models do not provide a sound basis for the treatment of hydrogen tunneling. A way out of this dilemma is the introduction of additional degrees of freedom. The spectroscopic barrier reflects the equilibrium configuration of all the atoms in the system except the moving hydrogen atom. In a molecule in thermal motion, deviations from equilibrium will occur and will affect the potential seen by the tunneling hydrogen. Thus, the spectroscopic and empirical barriers may be dynamically related as two instantaneous pictures of a fluctuating potential.

Although this description may seem qualitatively attractive, it does not hold much promise for quantitative work. To calculate the probability for the molecule to be in a particular configuration, one would need to introduce a potential governing the fluctuations. Therefore, it seems better to recognize from the outset that more than one dimension is required and use an appropriate multidimensional potential that will include the two equilibrium configurations corresponding to reactants and products.

In the usual adiabatic representation, these two configurations would be separated by a barrier. However, the eigenfunctions of such a double-well potential are delocalized over both wells and thus cannot be identified with the initial and final states of the transfer: instead it will be necessary to construct these states as superpositions of eigenfunctions.[14] Such a complicated construction is a far cry from the simple association of a rate law with a barrier shape. Moreover, even if carried through rigorously, the approach only yields an adiabatic approximation to the exact rate constant: it ignores non-adiabatic interactions between different potential energy surfaces.[4] Such interactions may be important in the transfer reactions at hand, where the barrier is due to the avoided crossing of two potential energy surfaces. If the two resulting surfaces remain close in energy near the top of the barrier of the lower surface, their non-adiabatic coupling should be included in the description.

It appears therefore that the conventional tunneling approach is both inaccurate and impractical and does not deserve its popularity. In the next sections we formulate an alternative approach that does not suffer from these disadvantages and allows a much more conclusive comparison with experiment.

2. Golden Rule Approach

The simplest quantum-mechanical method for describing the rate of a transition is time-dependent perturbation theory. The resulting expression takes on a particularly simple form in the case of a weak, time-independent interaction.[9] This case applies to virtually all hydrogen-transfer processes with rates slow enough to be measured with conventional kinetic methods, since the transfer frequency is generally very small compared to the vibrational frequency of typical hydrogenic modes. The transfer rate constant is then given by the golden rule[9]

$$k_{fi} = (2\pi/\hbar)|U_{fi}|^2\delta(\epsilon) \tag{3}$$

where U_{fi} denotes the interaction between the initial and final states, $|i\rangle$ and $|f\rangle$, with an energy difference ϵ. Thus, the δ function, $\delta(\epsilon)$, represents energy conservation; in actual calculations, it is replaced by a line shape function $\rho(\epsilon)$, e.g., a Gaussian or Lorentzian, such that $\rho(0)$ represents the density of final states $|f\rangle$ with the same energy as the initial state $|i\rangle$.

To calculate the transfer rate constant k_{fi}, we need a model for these states and their interaction. The model we shall use is a system of two molecules, A and B, of which A carries a hydrogen atom that B covets. For clarity, we give these molecules simple, specific properties: we assume that initially the hydrogen atom forms a CH bond in A and that B has a carbon atom with an unpaired electron. During an encounter between A and B, the hydrogen transfers from A to B, ending up in a CH bond of B, and A is left with a carbon atom with an unpaired electron. The

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[10] Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *Chem. Phys. Lett.* **1983**, *98*, 108.

[11] Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* following paper in this issue.

[12] McKinnon, W. R.; Hurd, C. M. *J. Phys. Chem.* **1983**, *87*, 1283.

[13] Le Roy, R. J.; Murai, H.; Williams, F. *J. Am. Chem. Soc.* **1980**, *102*, 2325.

[14] Brickmann, J.; Zimmermann, H. *J. Chem. Phys.* **1969**, *50*, 1608.

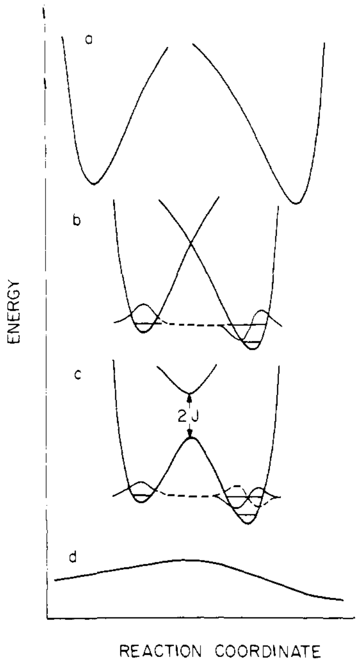

Figure 1. Basic potentials for the hydrogen tunneling problem. (a) Potential governing the hydrogen motion in the reactant (left) and in the product (right). (b) Potentials governing the hydrogen motion in the non-interacting system of reactants and products together with the localized wave functions representing the initial (left) and final (right) state in the transfer. (c) Potentials governing the hydrogen motion in the interacting system of reactants and products together with the delocalized wave functions representing the back-and-forth oscillation of the system between the resonant initial and final states. (d) An asymmetric Eckart potential of the type conventionally used to describe the transfer process represented by b and c.

initial and final potentials of the hydrogen are depicted in Figure 1a. To describe the hydrogen transfer, we combine these two potentials by simply adding them, as in Figure 1b, which represents the hydrogen potential in a pair of non-interacting molecules. In the absence of interaction, the initial and final potentials cross freely; we form the initial and final states by assigning the hydrogen to the left or right potential, respectively. Of course, without interaction there will be no transfer. The effect of an intermolecular interaction is included in Figure 1c: crossing is now avoided, the gap between the new upper and lower potentials being twice the coupling strength at the point where the potentials originally crossed. In the picture of Figure 1c, the hydrogen is no longer localized in the left or right well but spends time in both. For comparison we show in Figure 1d an Eckart barrier, a potential frequently used to interpret hydrogen tunneling data; its parameters are taken from an analysis of hydrogen abstraction by methyl radicals in a methanol glass.[13]

Formally, Figure 1c represents a Hamiltonian

$$H = H_A + H_B + J_{AB} \tag{4}$$

where H_A represents the left potential of Figure 1a,b, H_B the right potential, and J_{AB} the (intermolecular) coupling which leads to the difference between Figure 1b and Figure 1c. This Hamiltonian describes the behavior of the hydrogen atom in the field of the molecules A and B. This behavior will depend of course on the strength of the coupling, J_{AB}. We shall make the fundamental assumption that this coupling is weak, i.e., that the barrier height in Figure 1c is much larger than the vibrational level spacings in the two potentials H_A and H_B. This is the situation appropriate to hydrogen transfer between two carbon atoms but not necessarily between two oxygen or fluorine atoms for strong hydrogen bonds. If the coupling is weak, it can be treated profitably as a perturbation. The unperturbed system then consists of the non-interacting molecules, i.e., $H_A + H_B$, and the initial and final states are eigenstates of this zero-order Hamiltonian localized on H_A and H_B, respectively.

These states we denote by $\chi_v^A(r - \bar{r}_A)$ and $\chi_w^B(r - \bar{r}_B)$, where v and w are vibrational quantum numbers and $\bar{r}_A$ and $\bar{r}_B$ vibrational equilibrium positions. In the harmonic-oscillator approximation, their energies are given by $\epsilon_v = (v + {}^1/_2)\hbar\omega_A$ and $\epsilon_w = -\Delta H + (w + {}^1/_2)\hbar\omega_B$, respectively, where ω_A and ω_B are vibrational frequencies and ΔH is the exothermicity of the reaction. We assume that the two carbon atoms and the hydrogen atom are lined up so that the coordinate r connecting the A and B carbon atoms is also the CH vibrational and the C_AHC_B reaction coordinate. The functions χ_v^A and χ_w^B, corrected for anharmonicity, are illustrated in Figure 1b for $v = 0$ (zero-point motion) and $w = 1$, assumed to have the same energy as $v = 0$, i.e., for $-\Delta H + {}^3/_2\hbar\omega_B = {}^1/_2\hbar\omega_A$. They are eigenfunctions of H_A and H_B, respectively, and thus of $H_A + H_B$ in the absence of interaction. If we turn on the interaction J_{AB}, these localized functions no longer offer a complete description; however, we can easily form delocalized functions by taking linear combinations of the functions localized at A and B. In the case of Figure 1 where $\chi_0^A(r - \bar{r}_A)$ and $\chi_1^B(r - \bar{r}_B)$ are taken degenerate and J_{AB} is a small perturbation, the new wave functions may be written as

$$\chi_1^{\pm}(r) = 2^{-1/2}[\chi_0^A(r - \bar{r}_A) \pm \chi_1^B(r - \bar{r}_B)] \tag{5}$$

together with

$$\chi_0(r) = \chi_0^B(r - \bar{r}_B) \tag{6}$$

which has no degenerate component in the A molecule. The delocalized wave functions $\chi_1^{\pm}(r)$ are depicted in Figure 1c.

We are now in a position to formulate the matrix element governing the hydrogen transfer from A to B: the initial state is clearly $\chi_v^A(r - \bar{r}_A)$, the final state $\chi_w^B(r - \bar{r}_B)$, and the coupling must be J_{AB} so that

$$U_{fi} = U_{BA,wv} = \langle\chi_w^B(r - \bar{r}_B)|J_{AB}|\chi_v^A(r - \bar{r}_A)\rangle \simeq J_{AB}\langle\chi_w^B(r - \bar{r}_B)|\chi_v^A(r - \bar{r}_A)\rangle \tag{7}$$

where we have made the assumption that J_{AB} will not depend on the CH-stretching coordinate. This seems reasonable, since the interaction between A and B, at least the part of it relevant to the transfer, will be governed by interactions between the electrons at the carbons involved in the transfer; the small hydrogen 1s orbital will barely have an effect on the interacting carbon 2s and 2p orbitals. Thus, we can treat J_{AB} as a constant and need only calculate a vibrational overlap integral between wave functions center at $\bar{r}_A$ and $\bar{r}_B$; this overlap integral will thus be a function of $\bar{r}_A - \bar{r}_B$. If the vibrations are harmonic, the integral is easily calculated in analytic form, but even for the most complicated anharmonic potentials, it can be computed quickly.

The choice of the density of energy-conserving final states, $\rho_w(0)$, is governed by a consistency requirement as well as a practical argument. We need a manifold of final states dense enough to prevent back reaction, since only under these conditions does the golden rule apply.[6] Therefore we assume (subject to restrictions discussed in section 5) that the final state $\chi_w^B(r - \bar{r}_B)$ is embedded in a manifold of rotational, vibrational, and/or translational states which induce its rapid relaxation. This manifold is represented formally by the assignment of a line shape $\rho_w(\epsilon)$ to the final state. For practical reasons, we choose a Gaussian line shape with a half-width (at e^{-1}) equal to half the vibrational level spacing, $\Gamma = {}^1/_2\hbar\omega_B$; under these conditions the sum $\sum_w \rho(\epsilon_w - \epsilon_v)$ becomes a smooth function of the energy. The transfer rate constant for a given initial level v will then contain contributions from several levels w close in energy to v:

$$k_{BA}(v) = (2\pi/\hbar)J_{AB}^2\sum_w[\rho(\epsilon_w - \epsilon_v)|\langle\chi_w^B(r - \bar{r}_B)|\chi_v^A(r - \bar{r}_A)\rangle|^2] \tag{8}$$

The temperature dependence of the transfer rate constant is obtained by taking a thermal average over all possible initial states $\chi_v^A(r - \bar{r}_A)$ with energy ϵ_v

$$k(T) = \sum_v[k_{BA}(v)\exp(-\epsilon_v/k_BT)]/\sum_v\exp(-\epsilon_v/k_BT) \tag{9}$$

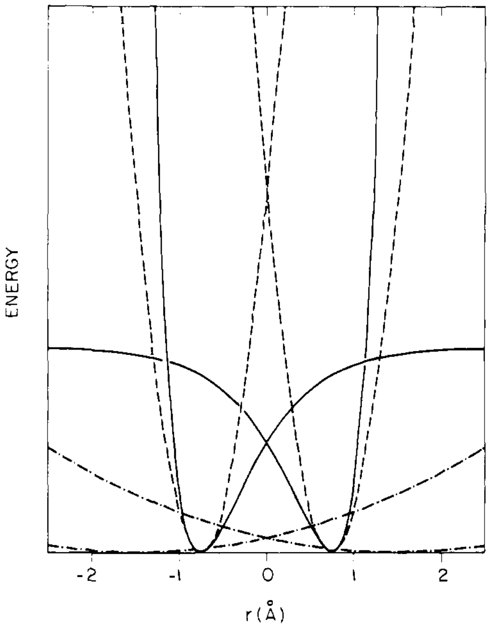

Figure 2. One-dimensional potential-energy models used to generate the transfer rate constants depicted in Figure 3. Dashed curves: harmonic potentials corresponding to CH-stretching vibrations; ω = 2960 cm^{-1}, $\bar{J}$ = 84 cm^{-1}, $\bar{r}_B - \bar{r}_A$ = 1.5 Å. Solid curves: Morse potentials corresponding to CH-stretching vibrations; parameters as above, together with X = 56 cm^{-1}. Dot-dashed curves: harmonic potentials adjusted to fit the experimental hydrogen transfer rate constants discussed in ref 10; ω = 300 cm^{-1}, $\bar{J}$ = 17 cm^{-1}, $\bar{r}_B - \bar{r}_A$ = 3.0 Å.

An increase in temperature leads to population of higher levels v with larger overlap integrals and therefore higher transfer rates. Isotope effects, such as those resulting from the replacement of hydrogen by deuterium, are obtained by changing the mass and frequency of the oscillators. Deuterium substitution reduces the overlap and thus the transfer rate. However, it also reduces the level spacing, leading to a more rapid increase of the rate constant with temperature for deuterium than for hydrogen tunneling. Hence qualitatively, the present formalism leads to the same overall predictions as the usual tunneling formalism.

3. Simple Solutions

We now consider quantitative results obtained by choosing specific values for the model parameters, in particular the form and separation of the two vibrational potentials. As a first example, we treat the simple case where these potentials are harmonic and identical, except for the separation $\bar{r}_B - \bar{r}_A$, assumed to be constant and positive. The corresponding potential energy diagram is depicted in Figure 2 (dashed lines): the reaction illustrated is symmetric as in the example $CH_4 + CH_3\cdot \rightarrow CH_3\cdot + CH_4$. This means that for sufficiently narrow levels in the final-state manifold, we need only consider "resonance" interactions characterized by $w = v$. To make this reaction irreversible, we would have to assume formally that the final states have a much higher density than the initial states. Since we take the interaction J_{AB} independent of the instantaneous position r of the hydrogen atom, we can evaluate $k(T)$ analytically for all temperatures. The result, derived earlier[4] in a different notation ($J_{AB}{}^2 = \kappa^2$, $\gamma = 2a^2$, $\hbar = \omega = \rho(0) = 1$), is

$$k(T) = (2\pi/\hbar)J_{AB}{}^2\rho(0)\exp[-\gamma - Z\exp(-\tfrac{1}{2}\beta\hbar\omega)]I_0(Z) \quad (10)$$

$$\gamma = (m\omega/2\hbar)(\bar{r}_B - \bar{r}_A)^2;\ Z = \gamma/\sinh(\tfrac{1}{2}\beta\hbar\omega) \quad (11)$$

In these expressions, m and ω are the reduced mass and the harmonic frequency of the oscillator, respectively, $\beta = 1/k_BT$, and $I_0(Z)$ is the zero-order modified Bessel function which is tabulated.[15]

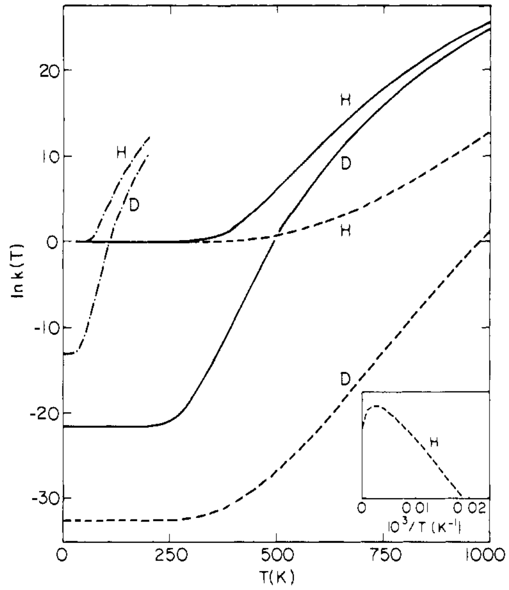

Figure 3. Hydrogen (H) and deuterium (D) transfer rate constants corresponding to the potentials depicted in Figure 2.

Typical plots of k against T and $1/T$, calculated with eq 10, are shown in Figure 3 as dashed curves. It is seen that these curves show three distinct regions: (i) A low-temperature region $k_BT << \hbar\omega$, where $k(T) = k(0)$. This limiting behavior follows directly from eq 10: in the limit $T \rightarrow 0$, we have $Z \rightarrow 0$ and $I_0(Z) \rightarrow I_0(0) = 1$ so that

$$k(T \rightarrow 0) = (2\pi/\hbar)J_{AB}{}^2\rho(0)\exp(-\gamma) \quad (12)$$

in agreement with the standard result

$$|\langle\chi_0(r - \bar{r}_A)|\chi_0(r - \bar{r}_B)\rangle|^2 = \exp(-\gamma) \quad (13)$$

for displaced harmonic oscillators in their lowest quantum state. (ii) A high-temperature region $k_BT \gtrsim \hbar\omega$, where, for $\gamma \gg 1$, we have $Z \gg 1$ and thus $I_0(Z) \rightarrow (2\pi Z)^{-1/2}\exp(Z)$, so that eq 10 reduces to

$$k(T \gtrsim \hbar\omega/k_B) = (\pi\beta\omega/\hbar\gamma)^{1/2}J_{AB}{}^2\rho(0)\exp(-\tfrac{1}{4}\beta\gamma\hbar\omega) \quad (14)$$

This equation has the same form as the Arrhenius equation, with two subtle differences. First, the frequency factor $A = (\pi\beta\omega/\hbar\gamma)^{1/2}J_{AB}\rho(0)$ is not temperature independent but proportional to $T^{-1/2}$. Second, the activation energy $E_a = {}^1/_4\gamma\hbar\omega$ is measured from the crossing point and not from the top of the adiabatic barrier which is ${}^1/_4\gamma\hbar\omega - J_{AB}$. (iii) A very-high-temperature region $k_BT \gg {}^1/_4\gamma\hbar\omega$, where the exponential in eq 14 goes to unity, so that

$$k(T >> \gamma\hbar\omega/4k_B) = (\pi\beta\omega/\hbar\gamma)^{1/2}J_{AB}{}^2\rho(0) \quad (15)$$

In this region $k(T)$ decreases slowly with increasing temperature.

In intermediate regions the curvature of $k(T)$ changes smoothly. The onset of temperature dependence can be estimated by comparing the squared zero-point overlap integral (eq 13) with the corresponding integral for the next higher level:

$$|\langle\chi_1(r - \bar{r}_A)|\chi_1(r - \bar{r}_B)\rangle|^2 = (1 - \gamma)^2\exp(-\gamma) \quad (16)$$

This integral starts to contribute significantly to $k(T)$ at a temperature T_0 such that

$$|\langle\chi_0(r - \bar{r}_A)|\chi_0(r - \bar{r}_B)\rangle|^2 \simeq |\langle\chi_1(r - \bar{r}_A)|\chi_1(r - \bar{r}_B)\rangle|^2\exp(-\hbar\omega/k_BT_0)$$

or, for $\gamma >> 1$,

$$k_BT_0 \simeq \tfrac{1}{2}\hbar\omega/\ln\gamma \quad (17)$$

For a hydrogen atom in a potential with a level spacing of 3000 cm^{-1}, tunneling over a distance $\bar{r}_B - \bar{r}_A$ = 1.5 Å, we have $\gamma \simeq 100$,

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[15] Abramowitz, M.; Stegun, I. A. "Handbook of Mathematical Functions"; *Natl. Bur. Stand. (U.S.) Circ.* 1964.

so that $T_0 \simeq 325$ K and $E_a \simeq 75000$ cm^{-1} according to eq 17 and 14.

These numbers are in strong disagreement with experiment. The tunneling reactions discussed previously,[10] which are typical of many hydrogen-transfer processes,[11] shown an onset of temperature dependence at $T_0 \simeq 50$ K, or at least far below room temperature. The observed temperature dependence does not follow the Arrhenius law (eq 1), but plots of ln $k(T)$ against $1/T$ would yield slopes corresponding to $E_a < 10000$ cm^{-1} near room temperature and still smaller values at lower temperatures. It follows that the model is completely unable to account for these observations.

An obvious oversimplification of the model is the use of harmonic potentials. Let us therefore repeat the calculation with Morse potentials (solid curves in Figure 2). The results are shown in Figure 3 as solid curves in units such that $k^{\mathrm{H}}(T = 0) \equiv 1$: both T_0 and E_a are reduced compared to the harmonic model but not nearly enough to account for the experimental observations, despite the fact that the anharmonicity parameter X $(=x_e\omega_e)$ used is that appropriate to the CH molecule[16] and thus probably an upper limit to the actual anharmonicity in typical C–H–C transfers. It is readily seen that further tinkering with the model parameters is not likely to bridge the large gap that remains between theory and experiment. The only way in which we can make the model account for the data is to abandon the spectroscopic definition of the parameters, i.e., to choose vibrational frequencies, anharmonicities, and intermolecular interactions without recourse to their actual values. Specifically, it would be necessary to take the frequency unphysically small and the anharmonicity and/or the interactions unphysically large. Only in this manner can one arrive at the empirical barriers previously found to reproduce the temperature dependence of tunneling rate constants.[5,10,11,13] An example of such a construction is illustrated by the dot-dashed curves in Figure 2; although the results depicted by dot-dash curves in Figure 3 are much better than those obtained with the other potentials of Figure 2, the parameters used in this construction are physically unacceptable, since they do not agree with the known properties of the reactants and products.

Nevertheless, this failure suggests a more promising approach. Clearly, lower-frequency vibrations are required to account for the observed values of T_0 and E_a, and since it is unphysical to eliminate the high-frequency CH-stretching modes, the solution appears to be to *add* low-frequency modes to the model. Such an approach, leading to the construction of a two-dimensional model, will be attempted in the next section.

4. Generalized Model

Although the preceding analysis shows convincingly that new degrees of freedom are required to reconcile theory and experiment, it does not identify the corresponding motions unequivocally. Two such motions are indicated. First, since in most transfer reactions the direction of transfer will not coincide with the (CH) stretching vibration, the contribution of bending modes should be considered. However, because of their high frequency, their contribution is not likely to account for the low-temperature onset of temperature dependence of the rate constants. Technically, the addition of a bending mode would turn the one-dimensional barrier into a two-dimensional saddle-shaped surface; this would require two-dimensional integration over non-separable coordinates: a substantial complication of the calculation. Second, instead of considering only modes involving hydrogen, we may include the thermal motion of the atoms or groups carrying the hydrogen. Such modes have much lower frequencies than the hydrogen modes and are thus more likely to give rise to temperature-dependent rate constants at low temperatures. Since they are also more likely to be separable from the CH-stretching modes than are the CH-bending modes, they are more easily handled: the corresponding two-dimensional integral would separate into two one-dimensional integrations. Hence we extend our model by including such a low-frequency vibration of the atoms between which the hydrogen is transferred.

This is not a new idea. Of course the relative motion of these atoms is always included in the analysis of gas-phase reactions such as $H_2 + H \rightarrow H + H_2$, since there would be no reaction without translational motion. But even in solids or inside molecules where the motion of these atoms is periodic, it is included occasionally in the description of tunneling reactions:[12,17-19] if this motion has a component along the reaction coordinate, it will clearly influence the transfer. Qualitatively, it will give rise to transfer through a barrier whose height and width are not constant but undergo low-frequency oscillations. It has been shown[12] that this oscillating-barrier model leads to rate constants whose temperature dependence is not that given by the Arrhenius equation (eq 1) but closely follows that of eq 2.

However, in the conventional tunneling approach, the introduction of such barrier oscillations remains somewhat problematic and has not found general acceptance. There are several ways of averaging the transfer rate over a barrier oscillation, which yield different averaged rates. The simplest answer is obtained if this oscillation is treated classically: in that case, eq 2 can be reproduced analytically. It may be objected, however, that a classical formulation should not be used in the description of a quantum phenomenon. Also, one expects on physical grounds that the vibration responsible for the barrier oscillations can change its degree of excitation during the transfer. This indicates that simple averaging over the oscillations will not be sufficient.

All these problems are avoided in our approach, in which the barrier oscillation enters simply as an additional degree of freedom. For a reaction in a solid medium or inside a molecule, it will be a vibrational mode involving the (carbon) atoms between which the hydrogen atom is transferred. The corresponding vibrations are represented by wave functions $\Lambda_V(R - \bar{R})$, where R is the component of the CC vibrational coordinate along the CHC reaction coordinate r, $\bar{R}$ its equilibrium value, and V a vibrational quantum number which may change into W during the transfer. In a linear CHC transition state, R is simply the instantaneous CC distance. For gas-phase reactions, $\Lambda(R)$ would describe a translational motion; for liquids, it would have to account for the relative motion of the two reacting molecules in a dense fluid medium. In the interest of simplicity, we restrict ourselves here to systems where $\Lambda(R)$ represents a vibration. We shall also assume that the wave functions $\Lambda_V(R - \bar{R})$ and $\chi_v{}^{\mathrm{A}}(r - \bar{r}_{\mathrm{A}})$ are adiabatically separable, i.e., that the interaction J_{AB} does not give rise to cross terms of the form rR in the potential.

Including this new degree of freedom, we generalize the transition matrix element U_{fi} from the form of (7) to

$$\begin{aligned} U_{\mathrm{fi}} = \langle \Lambda_W(R - \bar{R})\chi_w{}^{\mathrm{B}}(r - \bar{r}_{\mathrm{B}})|J_{\mathrm{AB}}|\chi_v{}^{\mathrm{A}}(r - \bar{r}_{\mathrm{A}})\Lambda_V(R - \bar{R})\rangle = \\ \langle \Lambda_W(R - \bar{R})|J_{\mathrm{AB}}S_{wv}(\bar{r}_{\mathrm{B}} - \bar{r}_{\mathrm{A}})|\Lambda_V(R - \bar{R})\rangle \quad (18) \end{aligned}$$

where

$$S_{wv}(\bar{r}_{\mathrm{B}} - \bar{r}_{\mathrm{A}}) = \langle \chi_w{}^{\mathrm{B}}(r - \bar{r}_{\mathrm{B}})|\chi_v{}^{\mathrm{A}}(r - \bar{r}_{\mathrm{A}})\rangle$$

Hence the overlap integral considered in the preceding section is now an operator since $\bar{r}_{\mathrm{B}} - \bar{r}_{\mathrm{A}}$ depends on R through[10]

$$R = \bar{r}_{\mathrm{B}} - \bar{r}_{\mathrm{A}} + 2\xi \quad (19)$$

where 2ξ is the sum of the two CH equilibrium separations, i.e., twice the CH bond length. This relationship is illustrated in Figure 4 for a linear model where motion along R corresponds to motion of the equilibrium positions $\bar{r}_{\mathrm{A}}$ and $\bar{r}_{\mathrm{B}}$ along the reaction coordinate r.

The dependence of J_{AB} on R is a quantum-chemical problem. Here we take a very simple approach and assume that J_{AB} is proportional to the overlap integral between the 2s and 2p orbitals

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[16] Herzberg, G. "Diatomic Molecules", 2nd ed.; Van Nostrand: Princeton, 1950.

[17] Tredgold, R. H. *Proc. R. Soc. London, Ser. A* **1962**, *80*, 807.

[18] Benderskii, V. A.; Goldanskii, V. I.; Ovchinnikov, A. A. *Chem. Phys. Lett.* **1980**, *73*, 492.

[19] Trakhtenberg, L. I.; Klochikhin, V. L.; Pshezhetskii, S. Ya. *Chem. Phys.* **1982**, *69*, 121.

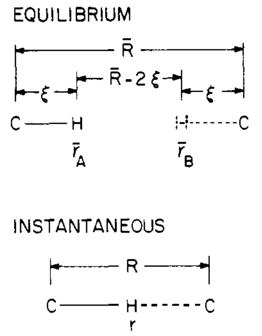

Figure 4. Relationship between the CH and CC vibrational (reaction) coordinates for a linear C–H–C transition state.

of the two carbon atoms involved in the transfer. We approximate this overlap by a simple exponential which leads to

$$J_{AB} = \bar{J} \exp[-\zeta(R - \bar{R})/a_0] \qquad (20)$$

where $\bar{J} \equiv J(\bar{R})$, the equilibrium value, ζ is an orbital exponent ($\simeq 1.625$ for carbon), and a_0 is the Bohr radius. Typically, J_{AB} varies more slowly with R than $S_{wv}(\bar{r}_B - \bar{r}_A)$, so that no drastic error would be introduced by setting $J_{AB} \simeq \bar{J}$.

The choice of the wave functions $\Lambda_V(R - \bar{R})$ will be dictated by the reaction at hand. If harmonic-oscillator wave functions are used, the integral can be evaluated analytically, but numerical integration will often be more practical. In that case more realistic potentials can be used without causing undue complications. The temperature dependence of $k(T)$ is now given by the thermal population of levels of both oscillators.

The actual calculation of $k(T)$ proceeds in three stages. First we calculate the rate constant for every combination of quantum numbers v, w, V, and W that is expected to contribute:

$$k_{BA,wWvV} = (2\pi/\hbar)\rho(\epsilon_w + \epsilon_W - \epsilon_v - \epsilon_V) \times |\langle\Lambda_W(R - \bar{R})|J_{AB}(R - \bar{R})S_{wv}(R - 2\xi)|\Lambda_V(R - \bar{R})\rangle|^2 \qquad (21)$$

where ϵ_V and ϵ_W are the energies associated with Λ_V and Λ_W, respectively, and ρ measures the density of energy-conserving states. Second, for any given combination v, V we sum over all relevant levels w, W:

$$k_{BA}(vV) = \sum_W \sum_w k_{BA,wWvV} \qquad (22)$$

Finally, we take thermal averages over v and V:

$$k(T) = \sum_V \sum_v \{k_{BA}(vV) \exp[-(\epsilon_v + \epsilon_V)/k_BT]\} \times \{\sum_V \sum_v \exp[-(\epsilon_v + \epsilon_V)/k_BT]\}^{-1} \qquad (23)$$

Strictly speaking, this result goes beyond the oscillating-barrier concept. In the older treatments, the transfer rate was simply averaged over the barrier oscillations, which were usually treated classically.[12,17] In our earlier note,[10] this averaging was done quantum mechanically; in terms of eq 21–23, this means that only diagonal elements $W = V$ were considered. This limitation was formally justified by assuming exact resonance between the levels v and w. In the present approach, all these restrictions are dropped, and the new degree of freedom is treated on the same footing as the reaction coordinate. Hence eq 21–23 describe two-dimensional tunneling.

The properties of these equations are illustrated for the system treated as an example in Figures 2 and 3. The reaction may be thought of as $CH_4 + CH_3\cdot \rightarrow CH_3\cdot + CH_4$, but the system is hypothetical in that rotations are neglected and arbitrary parameters are chosen for $\bar{R}$ and Ω, the frequency of the low-frequency mode. The results for this transfer and its monodeuterio analogue are shown by the solid curves in Figure 5 which are very similar to the dot-dashed curves of Figure 3. As expected, the introduction of a low-frequency mode leads to a much lower temperature T_0 for the onset of temperature dependence; the observed values of T_0 can now easily be accounted for in terms of reasonable values for the frequency Ω, e.g., $T \simeq 50$ K for $\Omega \simeq 200$ cm^{-1} in Figure 3. Also the plot of ln $k(T)$ against T for $T > T_0$ is quasilinear, in agreement with the pattern observed in many hydrogen-transfer reactions.[12] As shown earlier,[10] a simple version of eq 23 can account satisfactorily for the rate constants of two carefully studied examples of such reactions, without invoking unrealistic parameter values. We therefore conclude that eq 21–23 provide us with a new and promising tool to analyze hydrogen tunneling.

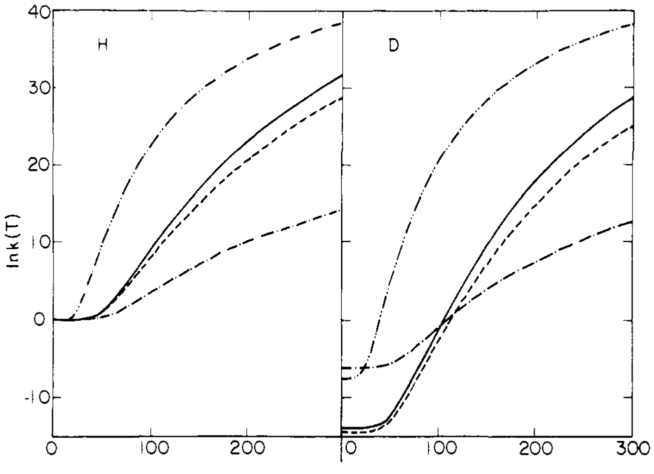

Figure 5. Illustration of the basic properties of the two-dimensional model: plot of ln k(T) against T for the following parameter values: $\omega = 2960$ cm^{-1}, $\bar{J} = 84$ cm^{-1}. Solid curves: $\Omega = 200$ cm^{-1}, $\bar{R} - 2\xi = 1.5$ Å, $\zeta = 1.625$. Dashed curves: same, except $\zeta = 0$ (i.e., constant coupling $J_{AB} = \bar{J}$). Dot-dashed curves: same as solid curves, except $\bar{R} - 2\xi = 1$ Å. Dot-dot-dashed curves: same as solid curve, except $\Omega = 100$ cm^{-1}.

To facilitate this analysis, we show in Figure 5 how $k(T)$ depends on the choice of parameter values. First, we show the effect of neglecting the R dependence of J_{AB} for two carbon atoms (dashed relative to solid curves): it is seen to be small, so that the assumption of a constant interaction is acceptable in semiquantitative work. Second, we show the effect of varying Ω-(dot-dot-dash relative to solid curves): a lower frequency for the CC mode leads to a lower onset temperature T_0, to larger slopes d(ln k)/dT at low temperatures, and to the intersection of the hydrogen and deuterium rate constant curves at a lower temperature as may be seen by superimposing the two halves of the figure. Third, we show the dependence of $k(T)$ on $\bar{R}$ (dot-dash relative to solid curves): a shorter tunneling distance reduces the slopes d(ln k)/dT and increases the relative rate of deuterium transfer.

5. Discussion

The present treatment of hydrogen transfer differs in two major respects from the usual treatment. First, it is based on the "diabatic" representation of Figure 1b rather than the "adiabatic" representation of Figure 1c. Treatments based on the latter representation generally invoke an adiabatic approximation; i.e., they neglect the upper potential energy surface and its non-adiabatic coupling to the lower surface. In the present, diabatic treatment, the coupling between the two surfaces, which cross freely in this representation, is adiabatic and can be fully included if it is weak enough to be treated as a perturbation. In the adiabatic representation, the eigenfunctions of the system are delocalized: they do not correspond to reactant or product wave functions but to linear combinations of them. In the diabatic representation, the localized reactant and product wave functions form the natural basis for describing the transfer. Hence, this representation has a number of practical advantages for the description of hydrogen transfer.

The second aspect in which our treatment differs from the usual approach is that it includes an additional degree of freedom, namely vibrational motion of the atoms between which the hydrogen atom is transferred. It is this motion that is principally responsible for the temperature dependence of the transfer reaction. The diabatic representation used allows us to include such additional degrees of freedom in a straightforward manner, namely by adding the corresponding wave functions to the initial and final states of the process and including the dependence of the coupling operator on the new coordinate. In the adiabatic approximation, on the other hand, the additional degree of freedom has usually been introduced as an oscillation of the barrier. In this approach, the two degrees of freedom are not treated equivalently, and off-diagonal matrix elements of the low-frequency oscillator are neglected.

In principle, our treatment can be further improved by including additional degrees of freedom. While it is not difficult to formulate such a generalized model, the parameters required for application to real systems are not normally available. The density-of-states function $\rho(\epsilon)$ implicitly includes additional motions, which are required to make the transfer irreversible, but these are treated in a much more approximate manner. The replacement of the corresponding vibrational structure by an unresolved broad band, namely a Gaussian in our case, will become strictly valid only in the limit of a very high level density which in practice will usually mean a large exothermicity. It is certainly not justified in the case of zero exothermicity where the transfer would be reversible. However, in practice one can usually measure only those reactions that are unidirectional and develop exponentially in time: in these cases the final state can always be represented by a continuum.

If the exothermicity is small, the density of states is roughly the same in the initial and final state. To simulate the effect of broadening of the initial state, we can add, as a third degree of freedom, a very low-frequency oscillation which affects the transfer indirectly by being coupled to the other oscillators. As a result, a single term in the two-mode model will now be represented by a sum of terms in the three-mode model, but the total contribution to the transfer will not change. The splitting will, however, affect the temperature dependence, namely at temperatures low enough to cause uneven population of the new manifold. At temperatures where adjacent levels of the new oscillator have virtually the same population, the effect of the splitting will be insignificant. At low temperatures, however, the transfer will not become temperature independent, as in the two-mode model, but retain a weak temperature dependence as long as $k(T)$ is above the level spacing of the third mode. It follows that for small exothermicities and low temperatures, we may expect significant deviations from the predictions of the model.

To gain further insight into its properties, we shall apply this model in the following paper in this issue[11] to a number of hydrogen-transfer reactions reported in the literature. In a future paper, we shall consider an extension of the model to three or more degrees of freedom. We believe, however, that in its present, simple form, the model can give a physically meaningful analysis of most hydrogen-transfer reactions in condensed systems.

Golden Rule Treatment of Hydrogen-Transfer Reactions. 2. Applications[†]

Willem Siebrand,* Timothy A. Wildman,[‡] and Marek Z. Zgierski

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6. *Received November 9, 1983*

Abstract: The model developed in part 1 (preceding paper) is applied to data ascribed in the literature to hydrogen (deuterium) tunneling. The transfer reactions considered are of the type $AH(D) + B \rightarrow A + H(D)B$, where A and B are carbon, nitrogen, or oxygen atoms attached to other atoms or groups. The model consists of crossing AH- and BH-stretching potentials together with an AB vibrational potential; the two vibrational motions are assumed adiabatically separable. Spectroscopic information is used to describe the AH and BH potentials. If A, H, and B are not collinear, the AH and BH frequencies are represented by linear combinations of bending and stretching frequencies according to fixed rules. The transfer distance, defined as the shortest distance between the two equilibrium positions of the hydrogen atom, is determined from molecular models. The AB potential and the coupling between the AH and BH potentials are treated as adjustable parameters, subject to restrictions determined by the nature of the transfer. Harmonic as well as anharmonic AB potentials are considered in the following applications to hydrogen and deuterium transfer reactions: (i) isomerization of 2,4,6-tri-*tert*-butylphenyl to 3,5-di-*tert*-butylneophyl; (ii) tautomerization to 2-methylacetophenone from the cis enol; (iii) 1,4-sigmatropic hydrogen transfer in a hexahydrocarbazole; (iv) hydrogen abstraction by free radicals in crystalline dimethylglyoxime; and (v) hydrogen transfer from dihydrophenanthrene to oxygen. Also briefly considered are (vi) hydrogen abstraction by methyl radicals in organic solids and (vii) tautomerization of *meso*-tetraphenylporphine. In general the rate constants for these reactions show a non-Arrhenius temperature dependence and a large deuterium effect. In most cases, the model can account successfully for these observations in terms of physically reasonable parameter values. Discrepancies are noted and traced back to limitations of the model in its present form, indicating directions for further development. The analysis leads to new insight into the mechanism of several of the reactions. It is concluded that the present treatment is physically more realistic and quantitatively more accurate than conventional tunneling treatments.

Part 1 of this series[1] describes a theoretical model developed to calculate rate constants for reactions in which hydrogen transfer occurs by tunneling, i.e., by a nonclassical mechanism. The model is not based on the conventional tunneling formalism, however, but on the golden rule of time-dependent perturbation theory. Correspondingly, the input parameters are not the height and width of the barrier through which the hydrogen atom tunnels but are vibrational parameters describing the initial and final states of the transfer process together with a coupling. The purpose of this reformulation is to make maximum use of the available spectroscopic information so as to reduce the arbitrariness of the description. An immediate consequence of this tightening of the

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[†] Issued as NRCC No. 23387.

[‡] Research Associate.

(1) Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.*, preceding paper in this issue.

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