

- (47) The fact that $\omega_{C(7)-C(8)}$ is larger (10.7°) than the diene angle of twist 7.8° is unusual. The effect of this is that the B ring is not diplanar and it possesses approximate C_5 symmetry with the mirror plane running through atoms C(6) and C(9). This does not affect the quadrant representation.
- (48) The assumed value is large compared to values used in calculations.^{3a,4} Since, according to our theory, a measured $\Delta\epsilon$ must always be smaller than the contribution of the diene alone and considering $\Delta\epsilon$ can be as large as 31 with values around 25 being common, we believe $\delta_{\text{diene}} \sim 40$ is reasonable.
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Tunneling Corrections to Unimolecular Rate Constants, with Application to Formaldehyde

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Abstract: Tunneling corrections to the rate constant for unimolecular reactions in an isolated molecule are treated within the standard transition state (i.e., RRKM) theory of such processes. The microcanonical distribution relevant to the unimolecular case causes tunneling effects to enter in a somewhat more complicated fashion than in the analogous transition-state theory for thermally averaged bimolecular rate constants; e.g., even within the separable approximation they do not enter as simply a multiplicative correction factor. Application of the theoretical expressions to some unimolecular processes ($H_2CO \rightarrow H_2 + CO$, *trans*-HCOH $\rightarrow H_2CO$) of interest in the collisionless photochemistry of formaldehyde indicates that tunneling effects are quite significant for rates of $10^9 s^{-1}$ or slower. Isotope effects are also considered and seen to be quite interesting.

Much has been written over the years about tunneling corrections to transition-state theory¹ for thermal rate constants of bimolecular reactions, but there has been little discussion about the effect of tunneling in the analogous transition state (i.e., RRKM) theory² of unimolecular reactions. The purpose of this paper is to consider such effects and to illustrate them by application to some processes of current interest in the photochemistry of formaldehyde.

Brief Summary of the Standard Transition State (i.e., RRKM) Theory for Unimolecular Processes

To simplify the presentation, rotational degrees of freedom will be ignored here; the Appendix shows how the formulas are modified to take proper account of total angular momentum conservation and other aspects of the rotational degrees of freedom. With this proviso, the standard expression² for the unimolecular rate constant (units s^{-1}) of an isolated molecule with total energy E is

$$k(E) = \frac{N(E)}{2\pi\hbar N_0'(E)} \quad (1)$$

where $N(E)$ and $N_0(E)$ are the integral densities of states for the transition state and for the reactant molecule, respectively. Specifically

$$N(E) = \sum_n h(E - \epsilon_n^\ddagger) \quad (2a)$$

$$N_0(E) = \sum_n h(E - \epsilon_n) \quad (2b)$$

where $h(x)$ is the usual step-function

$$h(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases}$$

and ϵ_n^\ddagger and ϵ_n are the vibrational energy levels of the transition state and the reactant molecule. In practice the vibrational energy levels are almost always assumed to be given by a separable harmonic oscillator approximation, so that

$$\epsilon_n = \sum_{i=1}^s \hbar\omega_i \left(n_i + \frac{1}{2} \right) \quad (3a)$$

$$\epsilon_n^\ddagger = V_0 + \sum_{i=1}^{s-1} \hbar\omega_i^\ddagger \left(n_i + \frac{1}{2} \right) \quad (3b)$$

where s is the number of vibrational degrees of freedom of the stable molecule, $\{\omega_i\}$ and $\{\omega_i^\ddagger\}$ are the normal mode frequencies of the reactant molecule and transition state, and V_0 is the "bare" barrier height, i.e., the energy of the saddle point of the potential energy surface (i.e., the transition state) relative to the minimum of the potential energy surface which corresponds to the reactant molecule. The total energy E is also defined relative to the minimum of the potential-energy surface.

Because of the large sums involved in computing the densities of states, it is customary in practice to approximate them by closed-form expressions. The simplest such approximation is the classical expression² which gives

$$N_0(E) = \frac{E^s}{s! \prod_{i=1}^s (\hbar\omega_i)} \quad (4a)$$

$$N(E) = \frac{(E - V_0)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} (\hbar\omega_i^\ddagger)} \quad (4b)$$

With these approximations eq 1 gives the simple classical rate expression²

$$k(E) = A \left(\frac{E - V_0}{E} \right)^{s-1} \quad (5a)$$

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where A is a frequency factor (units s^{-1}):

$$A = \left(\prod_{i=1}^s \omega_i \right) / 2\pi \left(\prod_{i=1}^{s-1} \omega_i \right) \quad (5b)$$

Modification to Include Tunneling

The only *simple* way to include the effect of tunneling along the reaction coordinate in transition-state theory is to assume that this degree of freedom—i.e., motion along the reaction coordinate—is *separable* from the other degrees of freedom; this approximation is also consistent with the use of eq 3 for the energy levels. Within the separable approximation tunneling is accounted for by replacing $N(E)$ in eq 1 by $N_{\text{QM}}(E)$ ¹

$$N_{\text{QM}}(E) = \sum_n P(E - \epsilon_n^\ddagger) \quad (6)$$

where $P(E_1)$ is the one-dimensional tunneling probability as a function of the energy E_1 in the reaction coordinate; in the classical limit of no tunneling $P(E_1) \rightarrow h(E_1)$, and $N_{\text{QM}}(E) \rightarrow N(E)$. The expression for the unimolecular rate constant which incorporates tunneling is thus

$$k_{\text{QM}}(E) = \frac{\sum_n P(E - \epsilon_n^\ddagger)}{2\pi\hbar N_0'(E)} \quad (7)$$

If the barrier along the reaction coordinate is approximated as an inverted parabola, then the tunneling probability is given by

$$P(E_1) = e^\epsilon / (1 + e^\epsilon)$$

with

$$\epsilon = 2\pi E_1 / \hbar\omega_b$$

where ω_b is the magnitude of the imaginary frequency related to the barrier. The generalized Eckart potential^{1a} in general provides a more accurate representation of the barrier, and in this case the tunneling probability is given by

$$P(E_1) = \frac{\sinh(a) \sinh(b)}{\sinh^2\left(\frac{a+b}{2}\right) + \cosh^2(c)} \quad (8)$$

where

$$\begin{aligned} a &= \frac{4\pi}{\hbar\omega_b} \sqrt{E_1 + V_0} (V_0^{-1/2} + V_1^{-1/2})^{-1} \\ b &= \frac{4\pi}{\hbar\omega_b} \sqrt{E_1 + V_1} (V_0^{-1/2} + V_1^{-1/2})^{-1} \\ c &= 2\pi \sqrt{\frac{V_0 V_1}{(\hbar\omega_b)^2} - \frac{1}{16}} \end{aligned}$$

V_0 is, as before, the barrier height relative to reactants, and V_1 is the barrier height relative to products; $V_1 - V_0$ is the exoergicity of the reaction (neglecting zero-point energies).

Equation 6 can be written in another form by the following manipulations:

$$\begin{aligned} N_{\text{QM}}(E) &\equiv \sum_n P(E - \epsilon_n^\ddagger) \\ &= \int dE_1 P(E_1) \sum_n \delta(E - E_1 - \epsilon_n^\ddagger) \\ &= \int_{-V_0}^{E-V_0} dE_1 P(E_1) N'(E - E_1) \\ &= \int_{-V_0}^{E-V_0} dE_1 P'(E_1) N(E - E_1) \quad (9) \end{aligned}$$

where $N(E - E_1)$ is the density of states defined by eq 2a; i.e.,

$N_{\text{QM}}(E)$ is given by a *convolution* of the classical approximation to it, namely, $N(E)$, and the tunneling probability. [For comparison, it is interesting to note that the tunneling correction factor Γ for a *thermally averaged* rate constant is given in terms of the tunneling probability by

$$\begin{aligned} \Gamma &= \int_{-V_0}^{\infty} dE_1 P(E_1) \frac{e^{-E_1/kT}}{kT} \\ &= \int_{-V_0}^{\infty} dE_1 P'(E_1) e^{-E_1/kT} \end{aligned}$$

One is *tempted* to use eq 9 with the approximation to $N(E - E_1)$ given by eq 4b, thereby obtaining the following simple expression for the tunneling rate constant:

$$k_{\text{QM}}(E) = A \int_{-V_0}^{E-V_0} dE_1 P'(E_1) \left(\frac{E - V_0 - E_1}{E} \right)^{s-1} \quad (10)$$

where A is the same frequency factor as above. It should be emphasized, however, that this is *not* a good thing to do. Although approximating $N_0(E)$ by eq 4a is valid (at least for the applications below³), in the threshold region where tunneling is important there are so few terms that contribute to the sum in eq 6 that eq 4b is a poor approximation to $N(E - E_1)$ in the integrand of eq 9. Equation 10 thus gives values much too large, and one must retain the discrete sum; since only a few terms do contribute to the sum, this causes no computational difficulties. The final expression we use (except for the modification due to rotation discussed in the Appendix) is thus

$$k_{\text{QM}}(E) = \frac{(s-1)! \prod_{i=1}^s \hbar\omega_i}{2\pi\hbar E^{s-1}} \sum_n P \left[E - V_0 - \hbar\omega^\ddagger \cdot \left(\mathbf{n} + \frac{1}{2} \right) \right] \quad (11)$$

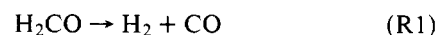
where

$$\begin{aligned} \mathbf{n} &= n_1, n_2, \dots, n_{s-1} \\ \omega^\ddagger \cdot \left(\mathbf{n} + \frac{1}{2} \right) &= \sum_{i=1}^{s-1} \omega_i \cdot \left(n_i + \frac{1}{2} \right) \end{aligned}$$

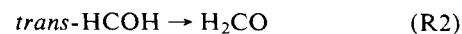
for the applications below the tunneling probability for the Eckart barrier (eq 8) was used.

Applications to Unimolecular Processes in the Ground Electronic State (S_0) of Formaldehyde

The motivation for this work has been the current interest in the photochemistry of formaldehyde,⁴ for which there are several potentially relevant unimolecular processes that can take place on the potential-energy surface of the ground electronic state (S_0). (The excited electronic state S_1 which is initially produced by laser excitation is assumed to undergo a radiationless transition back to S_0 .) Figure 1 shows a schematic of the potential energy surface⁵ for S_0 , and we consider the unimolecular decomposition of formaldehyde to molecular products



and the isomerization of the metastable species *trans*-hydroxymethylene—which has been suggested⁶ as the species first formed from S_1 —to formaldehyde:



Goddard and Schaefer⁵ have recently carried out extensive self-consistent field and configuration interaction calculations on formaldehyde and have determined all the parameters needed to evaluate the rate expressions given above. The energies of the two stable species (i.e., H_2CO and HCOH) and of the two transition states are shown in Figure 1, and Table I gives the six vibrational frequencies and three rotation con-

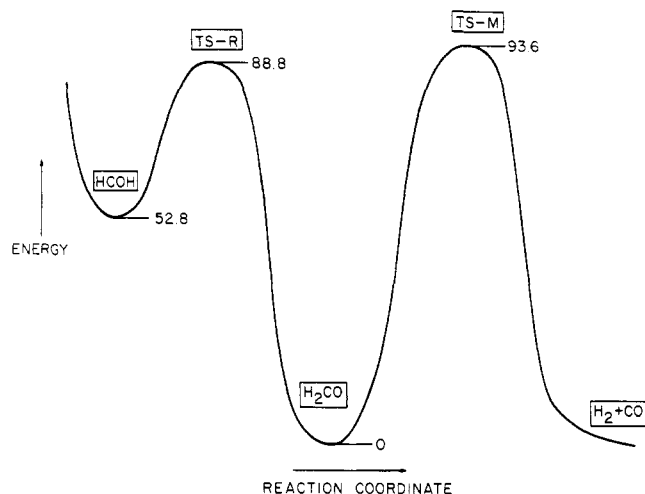


Figure 1. Schematic of the potential energy surface for the ground electronic state (S_0) of formaldehyde. Units of energy are kcal/mol, and the values shown are from the work in ref 5.

Table I. Vibrational Frequencies and Rotation Constants^a

Hydrogen Species			
H ₂ CO	<i>trans</i> -HCOH	TS-M	TS-R
2843	3634	2760	3675
2766	2684	1654	2803
1746	1595	1137	2339
1501	1264	941	1568
1247	1101	697	1221
1164	1093	2288 i	2299 i
1.13	1.04	1.05	1.09
1.30	1.16	1.18	1.25
9.41	10.52	9.06	8.86
Deuterated Species			
D ₂ CO	<i>trans</i> -DCOD	TS-M	TS-R
2160	2525	2186	2759
2056	1979	1503	2134
1700	1430	820	1735
1106	933	724	1408
990	921	505	974
938	799	1900 i	1675 i
0.88	0.84	0.76	0.89
1.07	0.97	0.89	1.10
4.70	6.28	5.45	4.75

^a The first six values are the vibrational frequencies, and the three values below it are the rotation constants. Units for all are cm^{-1} . TS-M and TS-R are the molecular and rearrangement transition states indicated in Figure 1.

stants for all four species. Unless stated otherwise, all rate constants given below were calculated from eq A.8, which for $J = 0$ is identical with eq 11, with the tunneling probability of eq 8.

Figure 2 shows the unimolecular rate constant for reaction R1 as a function of total energy E (relative to the bottom of the potential energy surface of H_2CO), and for comparison the classical rate constant is also shown (broken line). [The classical rates were all computed by direct state count of the transition state, i.e., from eq A.8 or 11 with the tunneling probability $P(E_1)$ replaced by the step-function $h(E_1)$.] The classical rate vanishes at the energy \tilde{V}_0 , the "bare" barrier height plus the zero-point energy of the transition state:

$$\tilde{V}_0 = V_0 + \sum_{i=1}^{s-1} \frac{1}{2} \hbar \omega_i \quad (12)$$

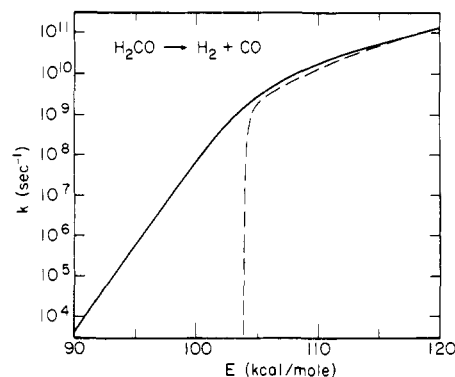


Figure 2. Unimolecular rate constant for the reaction indicated, as a function of total energy, for total angular momentum $J = 0$. The solid curve includes tunneling effects and is computed from eq 11. The broken curve is the classical rate, computed from eq 11 with the modification $P(E_1) \rightarrow h(E_1)$.

but one sees that tunneling allows a significant rate ($>10^9 \text{ s}^{-1}$) at this threshold energy. The rate has fallen only to 10^6 s^{-1} at an energy $\sim 8 \text{ kcal/mol}$ below \tilde{V}_0 . The exponential energy dependence of $k(E)$ (i.e., the linearity of the semilogarithmic plot) for $E < \tilde{V}_0$ also indicates that the process is dominated by tunneling in this region.

Figure 3 shows similar results for the rate constant of reaction R2, and one again sees that tunneling is substantial.

To assess the effect of rotation, calculations were also carried out for total angular momentum $J > 0$. The rate constant in general decreases with increasing J , but the effect is not large for the present examples: for $J = 10$, as large a value as is probably of interest, the rate constant for both reactions is decreased by a factor of ~ 2.5 at $E = 90 \text{ kcal/mol}$, and the factor decreases approximately uniformly to ~ 1.2 at $E = 120 \text{ kcal/mol}$.

Isotope Effects

Tunneling is significant for these reactions because they primarily involve the motion of hydrogen atoms, as evidenced by the large imaginary barrier frequencies $i\omega_b$ for the transition states in Table I. One thus expects large isotope effects in the tunneling region if H atoms are replaced by D atoms. The relevant frequencies (and rotation constants) for the deuterated species have also been determined by Goddard and Schaefer⁵ and are given in Table I.

Figure 4 shows the isotope effect, i.e., the ratio of the hydrogen to the deuterium rate constant for the two reactions. It is easy to see that the classical rate expression (eq 5) gives an energy-independent isotope ratio, and one sees in Figure 4 that this limit is approached for energies above the classical thresholds. In the threshold region and below, however, the isotope ratio is strongly dependent on energy: for energies significantly below the classical threshold there is an exponential energy dependence (i.e., the semilogarithmic plot is linear), but near the classical threshold itself the energy dependence is quite complicated, showing a pronounced *minimum*, in the vicinity of which the deuterium versions of the reactions are actually faster than the hydrogen versions.

Although comparing different isotopes at the same *total* energy (as in Figure 4) is the most meaningful comparison from a theoretical point of view, the experimental situation often dictates otherwise. Thus for formaldehyde the *excitation energies* from the ground vibrational state of S_0 to the ground vibrational state of S_1 are⁴ 80.6 kcal/mol for H_2CO and 80.9 kcal/mol for D_2CO , and since the zero-point energies of H_2CO and D_2CO are 16.1 and 12.8 kcal/mol, respectively, the *total* energies resulting from these vibrationless excitations are 96.7 kcal/mol for H_2CO and 93.7 kcal/mol for D_2CO . At these

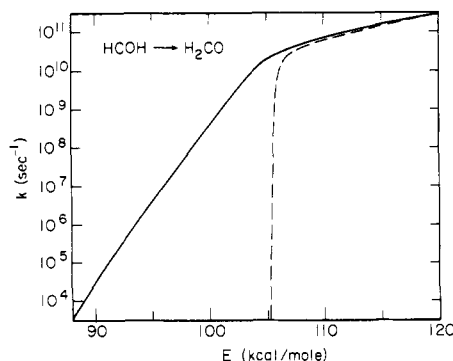


Figure 3. Same as Figure 2.

energies the present calculations give

$$k_1^H = 5.8 \times 10^6 \text{ s}^{-1}, k_1^D = 1.4 \times 10^5 \text{ s}^{-1} \quad (13a)$$

$$k_2^H = 1.9 \times 10^7 \text{ s}^{-1}, k_2^D = 5.7 \times 10^5 \text{ s}^{-1} \quad (13b)$$

where k_1 and k_2 refer to reactions R1 and R2, respectively. (The values for k_1^H and k_1^D in eq 13a include an extra factor of 2 due to symmetry, which has heretofore been omitted; this is because H_2CO and D_2CO have a twofold rotation axis and thus a symmetry number of 2.) These rates are for total angular momentum $J = 0$; for $J = 10$ they are all about a factor of 2 smaller.

Similar calculations have been carried out for the mixed isotope HDCO and the rates are, perhaps not unexpectedly, intermediate between those for H_2CO and D_2CO . For the vibrationless $S_0 \rightarrow S_1$ excitation, for example, the total energy is 95.3 kcal/mol and the rate of reaction R1 is

$$k_1^{\text{HD}} = 9.5 \times 10^5 \text{ s}^{-1} \quad (14)$$

Concluding Remarks

The main purpose of this paper has been to show how tunneling can be incorporated in the transition state (i.e., RRKM) theory for unimolecular reactions in a manner analogous to the way it is included in transition-state theory for thermal bimolecular reactions. Because the unimolecular case corresponds to a fixed energy rather than a fixed temperature, the effect of tunneling is somewhat more complicated; i.e., it does not enter as simply a multiplicative correction factor but rather in a more convoluted manner.

With regard to the applications to formaldehyde, one must be somewhat cautious regarding the specific values obtained for the rate constants because it is known that, when tunneling effects are substantial, the separable approximation for tunneling can be poor.^{1c} Nevertheless, the results obtained for the rates do indicate that, on the time scale of interest in the collisionless photochemistry of formaldehyde, i.e., 10^{-5} – 10^{-6} s, tunneling is likely to play a significant role.

Acknowledgments. I would like to thank Professors C. B. Moore and H. F. Schaefer for a number of stimulating discussions regarding the photochemistry of formaldehyde and their suggestion to consider the role of tunneling in unimolecular processes. Thanks are also due to Dr. J. D. Goddard and Professor Schaefer for providing the results of their extensive calculations on formaldehyde prior to publication. This work has been supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-Eng-48, and the Miller Institute of Sciences.

Appendix. Effect of Rotational Degrees of Freedom

There are three degrees of freedom associated with the overall rotation of a nonlinear molecule, the quantum numbers

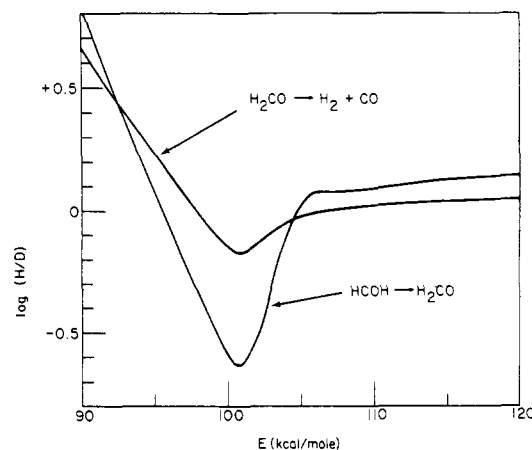


Figure 4. Isotope effects. Plotted is the logarithm of the ratio of hydrogen to deuterium rate constants for the reactions indicated, as a function of total energy.

for which we designate J , M_J , K . J , the total angular momentum quantum number, and M_J , its projection onto a space-fixed axis, are always conserved, while K is in general not conserved. (For a rigid symmetric top, K is also conserved.) One thus needs to define the unimolecular rate constant $k(E, J)$ which corresponds to a fixed value of total angular momentum J as well as total energy E ; because of the isotropy of space, the rate is independent of M_J .

We assume that K is a statistical degree of freedom, i.e., that it interchanges energy statistically with all the vibrational degrees of freedom. The unimolecular rate constant is then given by

$$k(E, J) = \frac{N(E, J)}{2\pi\hbar \frac{\partial N_0(E, J)}{\partial E}} \quad (\text{A.1})$$

where

$$N(E, J) = \sum_{K=-J}^J \sum_n h(E - \epsilon_{n,J,K}^\ddagger) \quad (\text{A.2a})$$

$$N_0(E, J) = \sum_{K=-J}^J \sum_n h(E - \epsilon_{n,J,K}) \quad (\text{A.2b})$$

$\{\epsilon_{n,J,K}^\ddagger\}$ and $\{\epsilon_{n,J,K}\}$ being the rotational-vibrational energy levels of the transition state and of the reactant molecule, respectively. In practice these energy levels are obtained by assuming a rigid rotor-harmonic oscillator approximation:

$$\epsilon_{n,J,K} = W_{J,K} + \sum_{i=1}^s \hbar\omega_i \left(n_i + \frac{1}{2} \right) \quad (\text{A.3a})$$

$$\epsilon_{n,J,K}^\ddagger = V_0 + W_{J,K}^\ddagger + \sum_{i=1}^{s-1} \hbar\omega_i^\ddagger \left(n_i + \frac{1}{2} \right) \quad (\text{A.3b})$$

where $W_{J,K}^\ddagger$ and $W_{J,K}$ are the rotational energies of the transition state and of the reactant molecule. Since the energy levels of most asymmetric rotors are reasonably well approximated by assuming an "almost symmetric top", we invoke that approximation here, so that⁷

$$W_{J,K} = \frac{1}{2} (A + B) [J(J+1) - K^2] + CK^2 \quad (\text{A.4a})$$

$$W_{J,K}^\ddagger = \frac{1}{2} (A^\ddagger + B^\ddagger) [J(J+1) - K^2] + C^\ddagger K^2 \quad (\text{A.4b})$$

where (A, B, C) and $(A^\ddagger, B^\ddagger, C^\ddagger)$ are the three rotation constants of the molecule and of the transition state. (A and B are chosen as the two most nearly equal rotation constants of the three A, B , and C , and A^\ddagger and B^\ddagger similarly.)

The sums over vibrational quantum number \mathbf{n} may be approximated as before,² but, because we consider cases of small J , the discrete sum over K is retained. Analogous to eq 4 the classical approximation to the sum over \mathbf{n} in eq 4.2 thus gives

$$N(E, J) = \sum_{K=-J}^J \frac{(E - V_0 - W_{J,K}^\pm)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} (\hbar\omega_i^\pm)} \quad (\text{A.5a})$$

$$N_0(E, J) = \sum_{K=-J}^J \frac{(E - W_{J,K})^s}{s! \prod_{i=1}^s \hbar\omega_i} \quad (\text{A.5b})$$

so that the classical rate expression which replaces eq 5a is

$$k(E, J) = A \frac{\sum_{K=-J}^J (E - V_0 - W_{J,K}^\pm)^{s-1}}{\sum_{K=-J}^J (E - W_{J,K})^{s-1}} \quad (\text{A.6})$$

A being the frequency factor of eq 5b. Note that, for $J = 0$, eq A.6 reduces to eq 5a.

The effect of tunneling along the reaction coordinate is included in the same manner as before, by replacing $N(E, J)$ by $N_{\text{QM}}(E, J)$:

$$N_{\text{QM}}(E, J) = \sum_{K=-J}^J \sum_{\mathbf{n}} P(E - \epsilon_{\mathbf{n}, J, K}^\pm) \quad (\text{A.7})$$

where again $P(E_1)$ is the one-dimensional tunneling probability. The expression for the tunneling rate constant which

generalizes eq 11 by including rotation is thus

$$k_{\text{QM}}(E, J) = \frac{(s-1)! \prod_{i=1}^s \hbar\omega_i}{2\pi\hbar} \times \frac{\sum_{K=-J}^J \sum_{\mathbf{n}} P\left[E - V_0 - W_{J,K}^\pm - \hbar\omega^\pm \cdot \left(\mathbf{n} + \frac{1}{2}\right)\right]}{\sum_{K=-J}^J (E - W_{J,K})^{s-1}} \quad (\text{A.8})$$

with the rotational energies $W_{J,K}$ and $W_{J,K}^\pm$ given by eq A.4. One notes that for the case $J = 0$ eq A.8 reduces to the result in the text (eq 11) that ignores rotation altogether.

References and Notes

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Substituent Effects on Strain Energies¹

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Abstract: Ab initio calculations employing the STO-3G basis set have been performed on numerous substituted derivatives of the strained (or unsaturated) molecules ethylene, cyclopropane, cyclobutane, acetylene, spiropentane, bicyclobutane, cyclopropene, tetrahydrene, and cubane. Substituents investigated include Li, BeH, BH₂, BH₃⁻, CH₃, CH₂⁺, CH₂⁻, CN, CF₃, NH₂, NH₃⁺, OCH₃, OH, O⁻, and F. Stabilization of strained molecules is achieved with σ -donating, π -withdrawing, and most π -donating substituents. σ withdrawal destabilizes unsaturated linkages. Effects decrease in the order of increasing saturation, e.g., ethynyl > vinyl > cyclopropyl. The stabilizing effects of Li and O⁻ substituents are particularly striking. The strain in tetralithiotetrahydrene is calculated to be less than one-fourth of that in tetrahydrene.

The concept of strain in small-ring organic compounds, originally introduced by Adolph von Baeyer in 1885, has remained fundamentally unchanged since its inception. It is generally accepted³ that (Baeyer) strain energy is associated with compression of bond angles at saturated carbon centers below the ideal tetrahedral angle. This view assumes electronic effects other than those resulting from angle bending to be unimportant; in particular it allows for no influence of substituents. This view is also implicit in the widely accepted group-increment scheme for calculating molecular heats of formation,⁴ in which the strain energy of a substituted small ring is taken to be equal to that of the unsubstituted parent. A recent, comprehensive review of strained molecules⁵ questions this view after examining the small body of available ther-

mochemical data on substituted ring systems. It is the purpose of this paper to supplement published data with quantities derived from theoretical calculations, and demonstrate that, contrary to the established view, appropriate substitution can indeed have dramatic effects on the magnitudes of strain energies.

Interactions between substituents and strained ring systems have been examined in other contexts. It has been noted^{6,7} that substitution on cyclopropane can result in changes in the geometry of the ring. Substitution at the 7 position of 1,3,5-tropyliene (**1a**) alters the position of the equilibrium with the more strained norcaradiene (**1b**) isomer.⁸⁻¹¹ Similarly, a substituent's electronic character determines whether it occupies the 1 or the 5 position on semibullvalene (**2**).^{11,12} Cy-