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Unimolecular Reactions at Low Energies and RRKM Behavior: Isomerization and Dissociation

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Rates of isomerization of electronically excited *trans*-stilbene and of the dissociation of isoquinoline–solvent complexes in jet beams are compared with those expected from RRKM theory as a function of energy; the comparison is made at low vibrational energies (~1200–3000 cm^{-1}). The jet result for the threshold energy of the isomerization is compared with the activation energy for the reaction in solution. The two values are in good agreement.

Introduction

With the picosecond-jet technique,[1,2] new data have emerged over the past several years on rates vs. excess vibrational energies in a number of different systems. These studies include isomerization, hydrogen bonding, intramolecular product formation, bond breakage of partially solvated molecules, and energy redistribution in aromatics like anthracene.[2] In several of these systems a *threshold effect*, discussed in ref 2, was found at low energies, typically 3–4 kcal/mol, for the rate constant (k) vs. excess energy (E_x). Since the molecule excited by the picosecond laser is vibrationally and rotationally cold (ca. 10–40 and 1–10 K, respectively), the real time measurements of k vs. E_x under supersonic jet expansion condition provide an opportunity to test a statistical theory of unimolecular reactions, such as RRKM, at low energies without complications from thermal energy congestion. Furthermore, because the laser excites well-defined modes, there is some hope for identifying k with the nature of the mode excited.

In this paper we analyze the threshold effect by using the RRKM theory and by utilizing the full vibrational modes in two particular systems: isomerization of stilbene, measured by Syage et al.,[3] and bond dissociation of solvated molecules reported recently by Felker and Zewail.[4,5] We then compare theory with experiment, and we provide some mechanism for a discrepancy, when present, when k is considered at different E_x's. Finally, the jet (and gas phase) results are compared with those obtained from solution phase studies, and a theoretical link between the two is made by using the appropriate thermal average. We also compare the RRKM calculations with a *classical* expression, and show that many orders of magnitudes discrepancy can be obtained if the same parameters are chosen for the total number of modes involved and the threshold energy. This result of the classical expression, as compared with the quantum one, is very well-known, albeit perhaps not universally recognized.

The Systems under Consideration

We consider here two systems. These are (a) the isomerization of *trans*-stilbene under isolated molecule conditions, and (b) the photodissociation of hydrogen-bonded complexes in the jet. For the latter we specifically refer to isoquinoline (IQ)–methanol and IQ–H_2O complexes.

For stilbene, when k was measured vs. E_x, the lifetime (2.7 ± 0.1 ns) at $E_x = 0$ showed a marked decrease to ~190 ps when $E_x \simeq 2600$ cm^{-1}. The apparent energy threshold was at ~1200 cm^{-1}. The barrier for isomerization[6] on the S_1 surface in solution ranges from 2 to 4 kcal/mol, and our 1200-cm^{-1} value shows this behavior very clearly (see Figure 1), and is consistent with theoretical calculations. Also, fluorescence and excitation spectra of *trans*-stilbene in the jet[3] display the torsional and low-frequency modes observed, and calculated by Warshel.[7]

The complexes[4,5] of IQ with water and alcohol were identified in the jet by their fluorescence spectra, excitation spectra, fluorescence lifetimes, and the dependence of their excitation spectra on solvent concentration. For the 1:1 complex, k vs. E_x was studied and, again, a threshold was found at ~3 kcal/mol (see Figure 2). The prominent low-frequency modes due to hydrogen bonding in the complexes were identified in the fluorescence spectra (typically less than 170 cm^{-1}).[4]

The RRKM Rates and the Calculation: Jets vs. Solutions

The simple RRKM theory predicts that

$$k(E_x) = \frac{N^\ddagger(E^+)}{h\rho(E_x)} \tag{1}$$

where $N^\ddagger(E^+)$ is the total number of quantum states of the transition state with energy less than E^+ (the difference between E_x and E_0, where E_0 is the threshold energy of a barrier). In our analysis E_0 is the difference in energies of the "reactant" and the transition state (zero-point energy levels). $\rho(E_x)$ is the density of states of the reactant at energy E_x. When thermal averaging is required, k must be averaged for the given temperature, T:

$$k(T) = \frac{1}{Q}\int_0^\infty k(E)\rho(E)e^{-E/k_BT}\,dE \tag{2}$$

where Q is the reactant's vibrational partition function and k_B is Boltzmann's constant. Combining eq 1 and 2, one obtains

$$k(T) = \frac{k_BT}{h}\frac{Q^\ddagger}{Q}e^{-E_0/k_BT} \tag{3}$$

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†Contribution No. 6826.

*Camille and Henry Dreyfus Foundation Teacher–Scholar.

(1) Wm. R. Lambert, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.*, **75**, 5958 (1981).

(2) For a review see A. H. Zewail, *Discuss. Faraday Chem. Soc.*, **75**/19 (1983).

(3) J. A. Syage, Wm. R. Lambert, P. M. Felker, A. H. Zewail, and R. M. Hochstrasser, *Chem. Phys. Lett.*, **88**, 266 (1982).

(4) P. M. Felker and A. H. Zewail, *Chem. Phys. Lett.*, **94**, 448, 454 (1983).

(5) P. M. Felker and A. H. Zewail, *J. Chem. Phys.*, **78**, 5266 (1983).

(6) For a review see R. M. Hochstrasser, *Pure Appl. Chem.*, **52**, 2683 (1980).

(7) A. Warshel, *J. Chem. Phys.*, **62**, 214 (1975).

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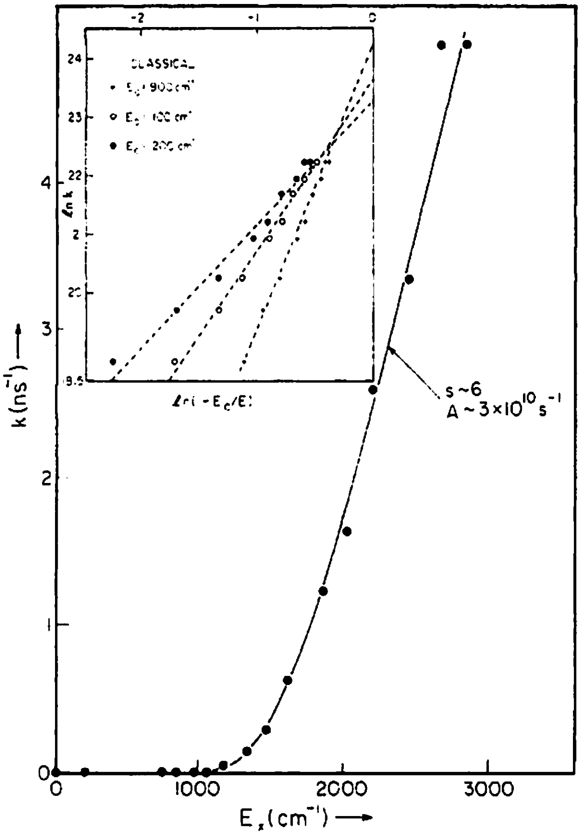

Figure 1. Observed[3] rates in stilbene. The solid curve is a fit obtained by using the classical theory with $E_0 = 900$ cm^{-1}. The best fit curve yields $s = 5.9$, $A = 3.2 \times 10^{10}$ s^{-1}. The inset shows classical fits with different E_0.

with $Q^{\ddagger}$ being the partition function of the transition state.

The parameters E_a and A in the well-known Arrhenius-type equation, $k_A(T) = A \exp(-E_a/RT)$, can be expressed in terms of $k(T)$ of eq 3, e.g., E_a equals $-\partial \ln k(T)/\partial(1/RT)$ and A equals $k(T)e^{E_a/RT}$. By this manipulation, we get

$$E_a = \bar{E}_0 + RT(1 - \xi)$$

$$A = \nu_R \frac{e^{1-x-\xi}}{\xi} \tag{4}$$

where $x = h\nu_R/k_BT$ and $\xi = x/(e^x - 1)$. In the limit of large T, A becomes ν_R.

In obtaining this expression, we assumed that the harmonic vibrational frequencies of the reactant state and the transition state are equal, except for the oscillator (a restricted internal rotation) that became the reaction coordinate (frequency ν_R). The threshold energy of the molecule, E_0 (cm^{-1} per molecule), is related to the molar value $\bar{E}_0$ (kcal mol^{-1}), by N_A (Avogadro's number). It is now clear that the solution phase activation energy E_a is related to the threshold energy. This point we shall address later when we compare theory with experiments.

To calculate k (i.e., $k(E_x)$), we used three methods for computing $N^{\ddagger}$ and ρ. These are direct counting of states, the Hase–Bunker program, and semiempirical calculations.

(i) The states were counted directly with as many as 22 frequency groups in a quantum stepping algorithm which we generated. In this case, the rotations were taken to be inactive, and the vibrations of the reactant and transition states were assumed to be the same (except for the reaction coordinate, of course) and harmonic. We also assume a "tight" transition state for simplicity.

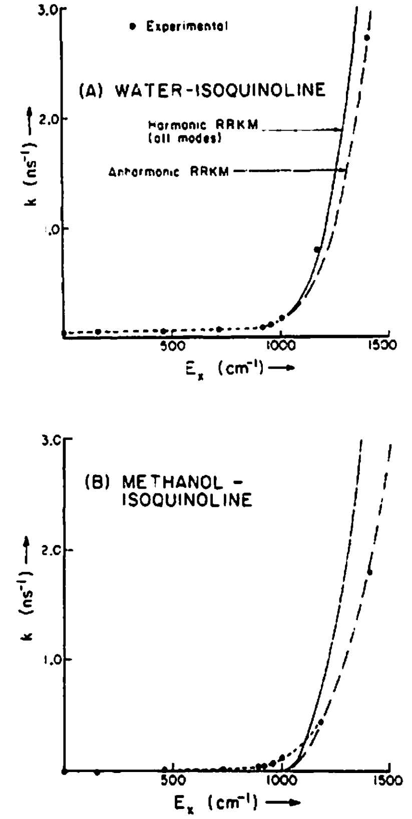

Figure 2. (a) Observed[4] and calculated rates for the IQ-H_2O complexes. Anharmonic corrections assumed $\langle D_e \rangle_{\text{molecule}} = 50$ kcal/mol and $\langle D_e \rangle_{\text{crit config}} = 15$ kcal/mol. (b) Observed[4] and calculated rates for IQ-MeOH complexes. Anharmonic corrections assumed $\langle D_e \rangle_{\text{molecule}} = 50$ kcal/mol and $\langle D_e \rangle_{\text{crit config}} = 10$ kcal/mol.

(ii) The Hase–Bunker program[8] we used allows only for frequency grouping into seven groups, and uses the same approximations of (i). Correction for anharmonicity involves our specification of an average dissociation energy.

(iii) For semiclassical calculations we used the Whitten–Rabinovitch[9] approximation for the density of states. This expression was available as an option in the Hase–Bunker program.

Comparison with Experiments

Isomerization. In Figure 3, we compare the experimental results of Figure 1, with calculations performed using our direct count of density of states, the count of the Hase–Bunker program, and the Rabinovitch–Whitten method. It is clear from the comparison that the calculations using these three different methods group together in a range of values for k vs. E_x, but are different from the experimental results by an order of magnitude (actually by a factor of 8.3, independent of the value of E_x).

A striking feature of these results is that the rates are slower, not faster, than RRKM rates. Had only a fraction of the degrees of freedom been active, the reverse would have been true.[10] Possible explanations for the lower experimental rates are (i) the reaction might be nonadiabatic, at a crossing of the trans and I (intermediate) po-

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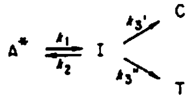
[8] W. L. Hase and D. L. Bunker, program QCPE-234, Caltech, Pasadena, CA.

[9] See, e.g., the book by P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York, 1972.

[10] B. J. Berne, N. De Leon, and R. O. Rosenberg, J. Phys. Chem., 86, 2166 (1982).

tential energy surfaces, with a nonadiabaticity factor of 8.3^{-1}, (ii) the energy may be trapped in certain coordinates in the transition state,[11] leading to a repeated crossing of the transition state by individual classical trajectories and, hence, to a rate below the microcanonical transition state (RRKM) values, (the degree of trapping is an unknown quantity) and (iii) in the isomerization there may be a reverse reaction from I to the trans compound. This last scheme is described below. In each case, the above effects may be minor in solution either because of collision-induced transfer from trans to I or because of rapid deactivation of I before it re-forms trans.

In the paper by Syage et al.,[3] a kinetic scheme was used to show that the shortening of the fluorescent lifetimes is related to the rate of the disappearance of *trans*-stilbene. Here, we shall take the following kinetic[12,15] model to account for the reversibility mentioned above:



$$A^* \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I \begin{cases} \xrightarrow{k_3'} C \\ \xrightarrow{k_3''} T \end{cases} \qquad (5)$$

The above reaction mechanism assumes that the disappearance of excited trans (A^*) is to some intermediate (I), and ultimately to ground-state cis (C) or trans (T). Because energy must be conserved, the intermediate can be "long-lived" and can feed back the excited trans[15] at a given E_x. Although one can solve the kinetic eq 5 exactly, for the sake of simplicity we shall assume a steady-state approximation for [I], i.e., $[\dot{I}] = 0$. (This implies that $k_1 < k_2 + k_3$.) Consequently, $\dot{A}^* = -k_3[I]$ for $t > 0$, where $k_3 = k_3' + k_3''$. Similarly $[\dot{C}] = k_3'[I]$, and $d[A^*]/d[C] = -k_3/k_3'$. It is therefore apparent from these solutions that

$$[A^*](t) = [A^*](0) \exp\left(-\frac{k_1 k_3}{k_2 + k_3} t\right) \qquad t > 0 \qquad (6)$$

and the quantum yield to form the cis isomer is given by $k_3'/(k_3' + k_3'')$. In the limit where $k_3 \gg k_2$, A^* decays with a rate constant k_1, as expected. On the other hand, if $k_2 > k_3$, then the experimental decay of A^* (still single exponential) will be with an apparent rate constant different from the RRKM k_1 by the factor $[k_3/(k_2 + k_3)]$. Also, if $k_3' \simeq k_3''$, the quantum yield will be 1/2.

With the above model in mind, we took the discrepancy between the calculated k_1 (RRKM) and the observed k (see Figure 4) to mean that

$$\frac{k_3}{k_2 + k_3} = \frac{1}{8.3} \sim 10^{-1} \qquad (7)$$

and, therefore, $k_2 > k_3$ (actually $k_2 \simeq 9k_3$). The fit of the data to the calculated RRKM after correction (using the results of the above model) is excellent (see Figure 4). We should also mention that using the same correction factor

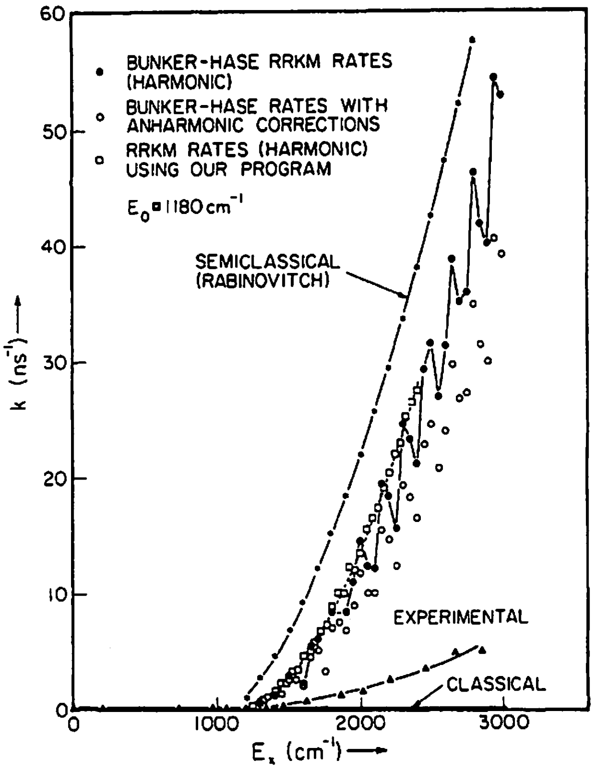


Figure 3. Experimental and various calculated rates. The classical predictions (on the abscissa) used s = number of normal modes with frequencies less than or equal to E_x, and $A = \nu_r$. The anharmonic rates assumed average dissociation energies $\langle D_e \rangle$ of 30 kcal/mol for the molecule and 100 kcal/mol for the critical configuration (transition state).

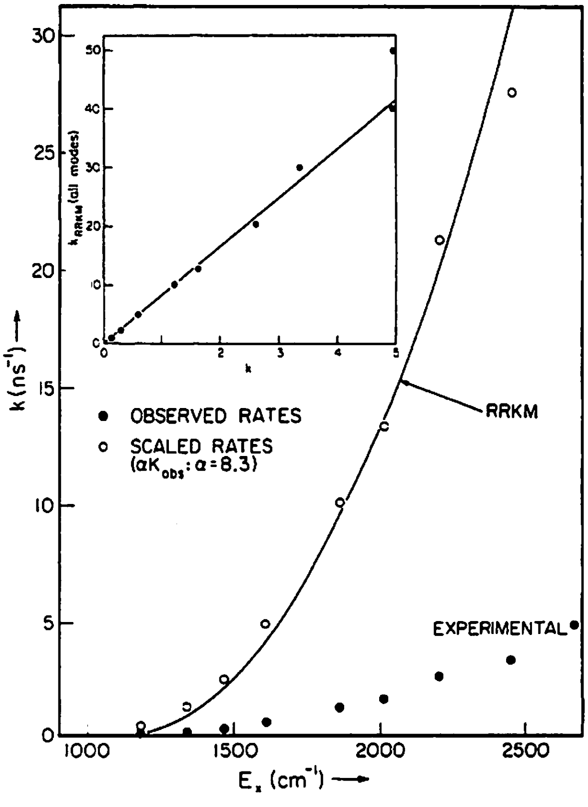


Figure 4. Scaled rates. Inset shows the best fit line for $k_{RRKM} = \alpha k$ in the range of $E_x \sim$ 1200 to 2700 cm^{-1}.

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(11) J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.*, 7, 616 (1939).

(12) For discussion of solution phase and high-pressure isomerization studies see ref 13 and 14.

(13) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 64, 94 (1968).

(14) J. Saltiel and J. L. Charlton in "Organic Chemistry", Vol. 42-3, P. deMayo, Ed., Academic Press, New York, 1980.

(15) We shall assume that, after vibronic excitation of the prepared state, there is a dephasing (within the lifetime) into a collection of states of the trans molecule, each with its own first-order rate constant for forming intermediate I. We assume that the range of values of such rate constants is narrow and clustered about the microcanonical value. Similarly, in the reverse step from I to trans, we assume rate constants from individual I states form a narrow range of rate constants clustered about the microcanonical one for this reverse reaction. In this reverse reaction, one forms, of course, not the initially prepared state but rather a collection of states of the trans molecule. At the E_x energies we are dealing with, we know that the redistribution is nearly complete: the fluorescence spectrum of the trans molecule at these E_x is highly congested, unlike its spectrum at lower E_x.

we obtained good agreement with the one data point obtained by Green et al.[16] for stilbene in a bulb ($T = 390$ K) excited at $E_x \sim 5500$ cm^{-1}. For this point, the thermal energy is less than E_x. For the other point at $E_x \sim 2600$ cm^{-1} measured by the same group we have a deviation of a factor of 1.8 after scaling, which we think is perhaps due to the fact that E_x is now closer to the thermal energy. (We are examining this point more closely by invoking an appropriate averaging scheme.)

We next examine the possibility, expressed in eq 6, that k_1 is much less than the sum of k_2 and k_3. We assume for simplicity that the vibrational frequencies of the reactant (A*) and the intermediate (I) are similar. We then have

$$\frac{k_1}{k_2} = \frac{\rho_2}{\rho_1} = \frac{\rho(E_x + \Delta E_0)}{\rho(E_x)} \qquad (8)$$

ΔE_0 is the difference in zero-point energy levels of A* and I, i.e., ΔE_0 is negative. Assuming $\Delta E_0 = -1.6$ kcal/mol, we find the calculated ratio k_2/k_1 varies from 10 to 7 for E_x's in the central part of the range, 1400 to 2500 cm^{-1}. Such small deviations reflect a relative insensitivity of k_2/k_1 to E_x.

Photodissociation of Solute–Solvent Complexes in the Jet. From the results of Figure 2 it is apparent that $E_0 \sim 2.9$ kcal/mol—the heat of association of quinoline and methanol in CCl_4 has been measured to be ca. 2.7 kcal/mol. Preliminary work showed the suitability of RRKM calculation to predict this threshold and the rate constants at two excess energies.[5] Using the RRKM calculation for k at all excess energies we obtained good fits for the rates when considering the six low-frequency modes for hydrogen bonding,[4] in addition to all modes of IQ below 1500 cm^{-1}. It is remarkable that the theory explains the dissociation process at this low energy. However, it should be mentioned that even at these low energies the density of states is very high (10^4/cm^{-1}) due to the presence of low-frequency modes (<170 cm^{-1}) characteristic of H bonding. The energy redistribution must be occurring with the help of these low-frequency modes for the bond to break and for k to be statistical in nature. Finally, the reverse rate constant k_2 in eq 5 is much less likely to be important in a dissociation than it is in an isomerization, particularly in an isomerization which is not highly exothermic.

Comparison with Solution Phase. For stilbene, since E_a and A are known in solutions, we used eq 4 to compare with our jet work assuming there are no specific different solvent interactions with A* and activated complex. Using a threshold energy of ~1100 cm^{-1} from the jet results we obtained E_a ($T \sim 234$ K) = 3.6 ± 0.6 kcal/mol[17] which compares with the experimental value of 3.5 ± 0.5 kcal/mol at an average $T \sim 234$.[18] The agreement is excellent and demonstrates that the threshold (jet) results for the isolated molecule can be compared with solution phase, and give the barrier height or the dissociation energy.

For the H-bonded isoquinoline–solvent complexes, using a threshold value of $E_0 \sim 1000$ cm^{-1} yields an E_a of 3.6 ± 0.4 kcal/mol[17] at room temperature (298 K). These results could not be compared directly with solution phase work because the only kind of data available in the literature are the thermodynamic parameters $\Delta H°$, $\Delta S°$, and $\Delta G°$. As a rough indicator of the reliability of our results, we compare our calculated E_a with the strength of H bonding in similar systems.[4,5,19]

Conclusions

The highlights of the results presented in this paper can be summarized as follows:

1. A statistical description of molecular (isolated) rate constants (RRKM) is applicable for the present experimental data,[4] at low average energies for systems with a high density of states at these energies.
2. Since the observed rates[3] for stilbene are lower than the simplest RRKM calculation we are forced to conclude that its vibrational phase space for the reactant is not restricted (i.e., all degrees of freedom are involved). Instead, we consider a reversible energy exchange between the reactant and the intermediate(s) involved to explain the reduced reaction rates. This does not exclude the other two possible mechanisms discussed in the text.
3. There is a theoretical and experimental connection between the value of the threshold energy for rates vs. excess vibrational energy and the solution phase activation energy.

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(16) B. I. Greene, R. M. Hochstrasser, and R. B. Weisman, *Chem. Phys.*, 48, 289 (1980).

(17) The error indicated reflects the uncertainty in our choice of the threshold energy.

(18) M. Sumitani, N. Nakashima, Y. Yoshihara, and S. Nagakura, *Chem. Phys. Lett.*, 31, 183 (1977).

(19) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand-Reinhold, New York, 1971, p 134.