THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 104, NUMBER 42, OCTOBER 26, 2000

ARTICLES

Non-Statistical Chemical Reactions: The Isomerization over Low Barriers in Methyl and Ethyl Cyclohexanones

Tomas Baer* and Alan R. Potts[†]

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received: January 12, 2000; In Final Form: August 24, 2000

At room temperature, methyl cyclohexanone exists in two dominant conformations in which the methyl group is either axial or equatorial to the six membered ring in the chair conformation. In addition to the axial and equatorial conformations, the ethyl cyclohexanones have several ethyl rotor positions. Both theoretical and experimental information indicate that the barriers for axial−equatorial and for the ethyl rotor interconversion are on the order of 4−5 kcal/mol. According to the transition state theory (TST), such low barriers lead to interconversion rates of 10^9 sec^{-1}. Yet, it has been demonstrated that the room-temperature concentrations are frozen out during the cooling in a pulsed supersonic expansion. This means that vibrational relaxation is much more rapid than interconversion of the various conformations. The analysis of the results indicates that the axial−equatorial or ethyl rotor interconversion rates must be at least 3 orders of magnitude less than predicted by the TST. It is proposed that at the low energies associated with these reactions, most of the vibrational oscillators are in their ground states in which the anharmonic coupling to other modes is minimal. As a result, intramolecular vibrational redistribution (IVR) is insufficient to permit this reaction to proceed at its statistically expected rate. It is also noted that the same reaction in solution phase appears to proceed at the statistical rate which suggests that the participation of the solvent modes enhances IVR.

Introduction

The transition state theory (TST) has been a remarkably robust theory that can account for experimentally observed rate constants of most chemical reactions.[1,2] Indeed, efforts to find reactions that violated the basic assumptions of this statistical theory have yielded only a few examples. The basic assumption in TST is that energy can freely flow among the vibrational modes of the molecule, an assumption that presupposes anharmonic coupling among the various vibrational modes. One of the few examples of incomplete coupling among the modes in a normal molecule was found by Rynbrandt and Rabinovitch[3] in the chemically activated reaction in which methylene reacted with hexafluorovinylcyclopropane to produce a bicyclic compound. Evidently the coupling between the two rings was insufficient to permit free energy flow in the time scale of the reaction. Consequently, activation of one of the rings results in the near exclusive ring opening of the activated ring rather than an equal reaction in both rings. Other examples of nonstatistical reactions have involved the dissociation of loosely bound dimers.[4,5] In molecules such as the HCN−HCCH dimer, the dissociation rates are orders of magnitude slower than predicted by the Rice Ramsperger, Kassel, and Marcus (RRKM) theory.[1]

Another class of reactions that has recently been suspected of reacting with nonstatistical rates is isomerization over low barriers. The trans-cis isomerization of stilbene in the first excited electronic state has been shown to proceed with rates that are slower than predicted by the RRKM theory.[6] According

---

[†] Present address: Bayer Corporation Pharmaceutical Division, West Haven, CT 06516.

10.1021/jp000173a CCC: $19.00

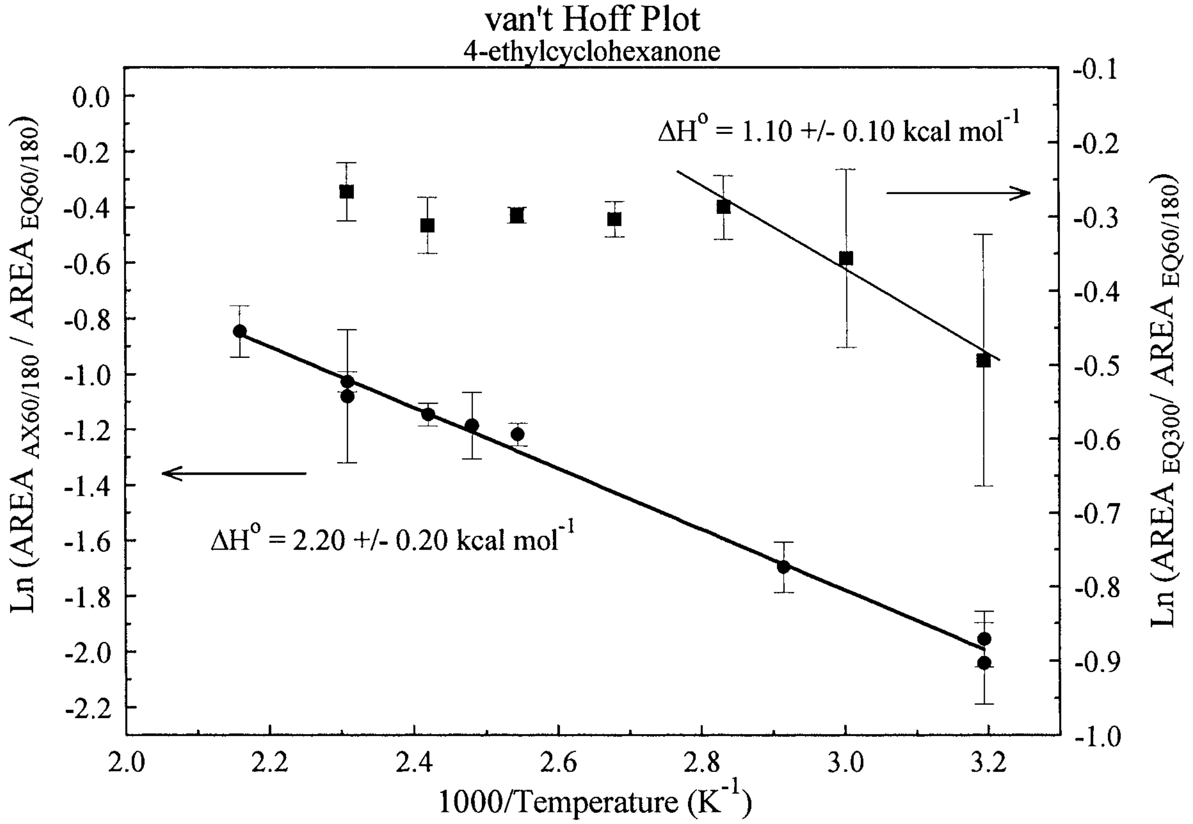

Figure 1. The van't Hoff plot for the equilibria between axial and equatorial ethyl groups (solid circles) and two ethyl rotor positions in the equatorial conformation for 4 ethylcyclohexanone (solid squares). The error bars are based on repeated measurements (at least three) of the spectra. Taken with permission from *J. Chem. Phys.* **1998**, *108*, 869.

to Leitner and Wolynes,[7,8] who analyzed these data in terms of a local random matrix theory, incomplete IVR reduces the isomerization rate. When this is taken into account, excellent agreement between measured and calculated rates over the 3.4 kcal/mol barrier was noted. McWhorter et al.[9] used an infrared microwave double resonance technique to investigate the isomerization rate of 2-fluoroethanol in which the barrier to isomerization of CH_2F group is only 2.6 kcal/mol (930 cm^{-1}). The rates, determined from the spectral peak widths, were found to be 3 orders of magnitude slower than predicted by RRKM, a finding supported by calculations of Leitner.[10] Finally, Borchardt and Bauer[11] have shown by gas phase NMR studies that the aziridine inversion is considerably slower than predicted by the statistical theory.

There are reasons to believe that these nonstatistical effects in the low barrier isomerization reactions of medium to large polyatomic molecules are not isolated instances. Spectroscopic studies of jet-cooled molecules that exist at room temperature in two or more conformations have repeatedly shown that the higher energy conformations freeze out in the course of the supersonic expansion. Among these systems are loosely bound van der Waals molecules such as $N_2O{-}HCN$,[12] $C_2H_2{-}HCN$,[4] and $CO_2{-}HCN$.[13] But the same holds for multiple conformations of normal molecules such as in ethoxybenzene,[14] 1,2-difluoroethane,[15] methyl-substituted cyclohexanones and tetrahydropyrans,[16] and di- and tripeptides.[17] Ruoff et al.[18] suggested on the basis of empirical observations that if the barrier to isomerization is greater than about 1 kcal/mol, the higher energy conformation will be trapped. The trapping of higher energy isomers by rapid vibrational cooling in the supersonic expansion can only occur if the vibrational relaxation rate, k_{cooling}, is faster than the isomerization rate, k_{isom}, from the higher to the lower energy isomer. Although these studies have generally not determined what fraction of the higher energy population remains in the supersonically cooled molecular beam, the magnitude of the signal attributed to the higher energy population is sufficient to conclude that in these systems $k_{\text{cooling}} \geq k_{\text{isom}}$. This paper will demonstrate that this inequality can be correct only if k_{isom} is much less than predicted by the RRKM theory.

During the past few years, we have carried out a series of experiments in which the temperature of the gas in the nozzle prior to expansion was varied between room temperature and 200 °C.[19-21] The sample consisted of axial and equatorial isomers of 3- and 4-methyl cyclohexanone and 4-ethylcyclohexanone. In the case of the 4-ethyl cyclohexanone, the ethyl rotor could also reside in two unique rotor orientations. The population of the various isomers was monitored by 2+1 resonance enhanced multiphoton ionization (REMPI) spectroscopy of the cold gas some 5 cm downstream from the nozzle. With backing pressures in excess of 400 Torr Ar, no evidence of hot bands was noted, thus indicating an internal temperature of less than 50 K. Raising the pulsed valve temperature has the effect of increasing the population of the higher energy isomer by an amount that depends on the $\Delta H°$ of isomerization. This enthalpy difference can be determined from the slope of a van't Hoff plot (log K_{eq} vs $1/T$). In this paper, we analyze the consequences of these results in terms of the rates of vibrational cooling and the rate of isomerization.

The Experimental Results

Figure 1 shows the previously reported van't Hoff plot for the axial−equatorial equilibrium as well as the ethyl rotor equilibrium for 4-ethyl cyclohexanone.[20] This molecule has two chair forms, the lower energy form being associated with an equatorial ethyl group. When the ring flips, this ethyl group is converted into the energetically less favorable axial orientation. For each orientation of the ethyl group (equatorial or chair), the ethyl group can also rotate. Because of symmetry in the 4-ethyl cyclohexanone, each ethyl group orientation has just two distinct rotor minima.[22] Three unique conformations are observed in the REMPI spectra. These are the two rotor conformations with the ethyl group in the equatorial orientation, and just one rotor conformation with the ethyl group in the axial orientation. The second rotor orientation is too sparsely populated to be observable. The van't Hoff plot in Figure 1 was obtained by plotting the logarithm of the peak area ratios, ln[Ax/Eq] and ln[Rotor1_{eq}/Rotor2_{eq}] as a function of T^{-1}. The data were collected by scanning the laser through the two absorption peaks at least three times at each temperature. The error bars in the figure are based on these repeated measurements of the peak areas. The pulsed valve was allowed to equilibrate for at least 45 min before recording the spectra to ensure that the temperature, measured by a thermocouple attached to the nozzle orifice, was constant. A complete data set required about 16 h. This was repeated in order to establish reproducibility of the results. Similar data have obtained for 3-methyl cyclohexanone,[21] 4-methyl cyclohexanone,[20] 3-methyltetrahydropyran,[23] and 3-methylcyclopentanone.[24]

The van't Hoff plot associated with the axial−equatorial equilibrium in Figure 1 is linear up to the highest temperature investigated (ca 200 °C). The fact that this plot is linear indicates that the cooling of the two isomers is much faster than the rate of equilibration of the axial and equatorial conformations. In the limit of very high temperature, the isomerization rate must overtake the cooling rate because the former increases as exp($-1/T$), while the latter, according to the SSH theory,[25] increases only as exp($-1/T^{1/3}$). When this happens, the two conformations will equilibrate during the cooling process in the molecular beam expansion. This equilibration will continue during the expansion until the cooling process finally freezes the conformations. This would result in a van't Hoff plot that levels off at high temperature. This is not observed in the case of the axial−equatorial equilibrium.

The van't Hoff plot associated with the ethyl rotor motion, on the other hand, exhibits precisely the type of behavior expected if the isomerization rates overtake the vibrational cooling rates as the temperature is increased. The break in the plot at about 80 °C is the temperature at which the ethyl rotor rate becomes faster than the vibrational cooling rate. While it might be argued that the error in the data do not support a clear break at 80 °C, the main point is the flat van't Hoff plot at high energies which shows that the ethyl rotor motion is clearly more rapid than the vibrational cooling rate so that at the higher temperatures the higher ethyl rotor state equilibrates to the lower energy form until it finally freezes out at some finite temperature. Because there is only one vibrational cooling rate for the two conformations of this molecule, we conclude that ethyl rotor motion is considerably faster than the axial−equatorial equilibration rate.

Figure 2 shows a potential energy diagram for axial−equatorial or the ethyl rotor interconversion (they have about the same barrier height). It also shows the thermal ro-vibrational energy distribution at 300 and 400 K for ethyl cyclohexanone. This distribution extends well above the barrier. The finding that the vibrational cooling in the molecular beam is faster than the isomerization rate is thus surprising.

Energetic Considerations. To calculate the rate of isomerization, we need to know the activation energy as well as the vibrational frequencies of the ground and transition states. These were determined for the ethyl rotor and the axial−equatorial interconversion reactions by both molecular mechanics and Hartree−Fock molecular orbital calculations. The calculated and experimental values for the transition state energy E_{TS} and the $\Delta H°$ of isomerization are shown in Table 1. Figure 2 defines these parameters.

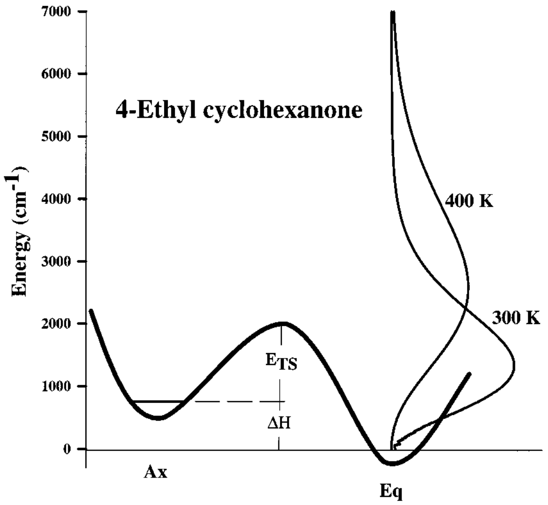

Figure 2. The schematic potential energy diagram for isomerization of axial and equatorial conformations as well as the ethyl group rotation in 4-ethyl-cyclohexanone. The thermal ro-vibrational energy distribution at 300 and 400 K are also indicated in which the reaction coordinate axis also serves as the population for the internal energy distribution.

TABLE 1: Energetic and Entropic Parameters for Isomerization Reactions in 4-Ethylcyclohexanone

	energy or enthalpy in kcal mol^{-1}			$\Delta S^{\ddagger}$ (cal/mol-K)[a]		
	mol. mech.	ab initio[a]	expt	90 K	300 K	500 K
ax-equatorial (E_{TS})	4.0	4.0	4.0[b]	−0.8	−3.0	−3.9
ethyl rotor (E_{TS})	3.5	4.0	3.5[c]	−2.1	−4.6	−5.6
ax-equatorial $\Delta H°_{0K}$	1.84	2.1	2.2			
ethyl rotor $\Delta H°_{0K}$	1.0	1.1	1.1			

[a] Hartree−Fock calculations with a 6-31G* basis set. [b] Anet et al. (1973) based on cyclohexanone.[26] [c] Based on adjustment of the measured barrier in 2,2 dimethyl butane Wiberg and Murcko (1988).[27]

The experimental value for the activation energy of Anet et al.[26] is based on a low temperature NMR experiment with partially deuterated cyclohexanone in which the 4-position had one H and one D atom. A direct experiment with methyl or ethyl cyclohexanone is difficult to perform because the rather large ΔH causes the higher energy axial group to be minimally populated at a temperature of −184 °C. On the other hand, the ΔH for the partially deuterated sample with the D atom positioned in an equatorial or axial orientation is nearly zero, thereby populating the two isomers equally even at low temperatures. The rate of ring inversion was determined by modeling the NMR low-temperature spectra. They found a rate of 130 s^{-1} at −184 °C (90 K). This rate constant can be expressed in terms of the transition state theory:

$$k(T) = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \qquad (1)$$

from which Anet determined that the $\Delta G^{\ddagger}$ is 4.1 kcal/mol. Our own calculations of the entropy of activation determined from the calculated vibrational frequencies of the ground and transition states yields a $\Delta S^{\ddagger}$ (90 K) of just 0.8 cal/mol-K. This results in an enthalpy of activation of 4.0 kcal/mol. Is such a value applicable to methyl or ethyl cyclohexanone? A major difference lies in the fact that the partially deuterated cyclohexanone has a ΔH of zero because it is a symmetric process. The presence of the methyl or ethyl group raises one of the wells by 2 kcal/mol. This should have the effect of reducing the axial → equatorial barrier somewhat. On the other hand, the bulkier methyl or ethyl group should raise the barrier. A value of 4 kcal/mol for the axial−equatorial barrier thus seems reasonable for methyl and ethyl cyclohexanone.

The ethyl rotor barrier in ethyl cyclohexanone has not been determined experimentally. However, the barrier to ethyl rotation in 2,2 dimethyl butane was investigated by variable temperature NMR[27] and found to be 5 kcal/mol. The 2,2-dimethylbutane molecule is not the appropriate model for ethyl cyclohexanone because it contains an extra methyl−methyl group interaction. A better model would be 2-methyl butane. However, no data are available for it. According to Eliel et al.,[28] the barrier in 2-methyl butane should be about 1.5 kcal/mol less than in 2,2, dimethyl butane. Thus, an experimental value adjusted by empirical corrections yields an ethyl group rotational barrier of about 3.5 kcal/mol.

The Statistical (TST) and RRKM Isomerization Rate Calculations. Table 1 shows that the activation energies, the reaction enthalpies, and the entropies of activation are similar for the ethyl rotor motion and the axial−equatorial interconversion reactions of both methyl and ethyl cyclohexanones. According to the transition state theory (TST) in eq 1, it can be expected that their reaction rate constants will also be similar. The high-pressure TST rates for axial−equatorial and ethyl rotor isomerization using the data in Table 1 (4 kcal/mol for axial−equatorial interconversion and 3.6 kcal/mol for the ethyl rotor barrier) suggest that the room temperature (298 K) rates for both reactions should be about 1.7×10^9 sec^{-1}. At 500 K, near the upper range of the experimental results, the rates would be 2.7×10^{10}, and 1.7×10^{10} sec^{-1} for the axial−equatorial and ethyl rotor interconversions, respectively.

We can also calculate microcanonical rates as a function of the internal energy using the RRKM equation

$$k(E) = \frac{N^{\ddagger}(E - E_o)}{h\rho(E)}$$

in which $N^{\ddagger}(E-E_o)$ is the sum of internal energy states from 0 to $E-E_o$, E_o is the activation energy, h is Planck's constant, and ρ(E) is the density of internal energy states at an energy E. The results of this calculation are shown in Figure 3. As will be shown in the following section, cooling in the molecular beam expansion requires about 1 μs, thus apparently providing sufficient time to equilibrate the isomers.

Vibrational Relaxation Rates. While simple theories are available for the determination of unimolecular reactions (TST and RRKM), no simple theory has been developed for calculating the bimolecular vibrational relaxation rate of a polyatomic molecule. On the other hand, considerable progress has been made in the experimental determination of energy transfer from highly excited large molecules.[29] In all cases, the results show that the amount of vibrational energy transferred per collision is relatively small. For instance, in the case of pyrazine excited to 5 eV (40 000 cm^{-1}) of internal energy, Michaels et al.[30] found that only 2.5% of the total energy (1000 cm^{-1}) was transferred to the colliding CO_2 molecules per collision. The fraction transferred is expected to decrease as the internal energy of the molecule is reduced. Sound velocity dispersion experiments at room temperature showed that in a molecule such as cyclopropane, the energy transferred per collision is just 2 cm^{-1}.[31]

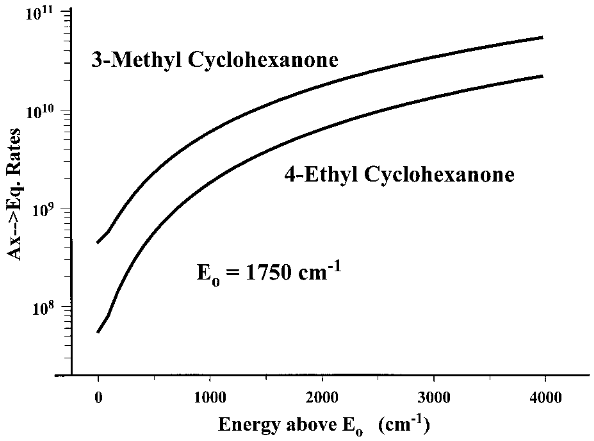

Figure 3. The RRKM calculated rate constants for isomerization of axial to equatorial groups in 3-methyl cyclohexanone and 4-ethyl cyclohexanone with an assumed barrier of 1750 cm^{-1}.

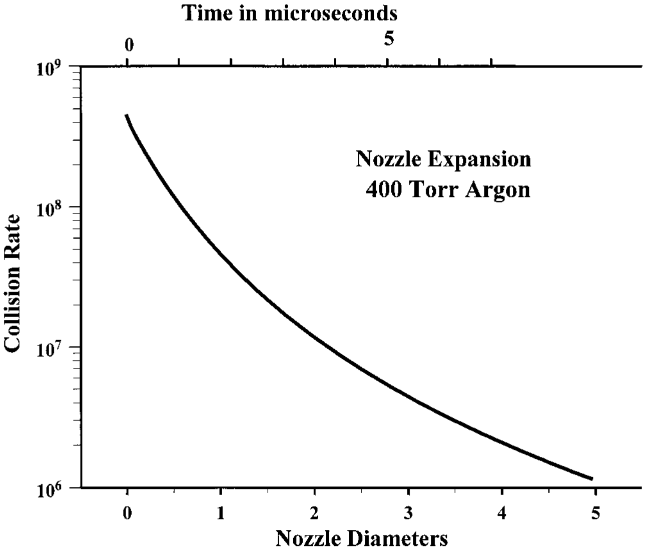

Figure 4. The hard sphere collision rate of Ar gas expanded from a nozzle with a stagnation pressure of 400 Torr. The collision rate calculated using information provided by Miller (ref 32) is given in terms of the nozzle diameter (0.5 mm) and the time in microseconds.

Although we are not in a position to calculate the vibrational energy transfer rate from ethyl cyclohexanone to the Ar bath gas at temperatures below 298 K, we can determine an upper limit, which is given by the collision frequency. In the pulsed expansion of a gas, the collision frequency decreases from its value at the stagnation pressure and temperature of 400 Torr and $298 < T < 450$ K to nearly 0 at the end of the expansion when collisions effectively cease because the gas density is very low and the temperature has reached its limiting low value. Both the gas density and the temperature can be calculated as a function of the distance from the nozzle orifice for the case of a rare gas expansion. Because our sample consists of 95% Ar and 5% sample, the density and temperature can be approximated by use of the rare gas equations.[32] The results of this calculation are shown in Figure 4 as a function of the nozzle diameter or time. This collision rate can be contrasted to the RRKM calculated isomerization rates as a function of the energy above the isomerization limit. It is evident that the statistical theory rate constants are higher than the collision frequency at 400−500 Torr pressure, which means that this reaction is predicted to be in the falloff region.

Discussion

A comparison of Figures 3 and 4 shows that the calculated isomerization rates are orders of magnitude higher than the collision rates. Because the collision rates are upper limits of the vibrational cooling rates, the discrepancy between the calculated isomerization rates and the vibrational cooling rates would be even greater than those illustrated in Figures 3 and 4. This is in sharp contrast to our experimental findings which indicate that the isomerization rates should be smaller than the vibrational cooling rates. If we take the average collision rate in the first μs to be about 3×10^8 sec^{-1} and note that $k_{\text{cooling}} < 3 \times 10^8$ sec^{-1}, the experimental results indicate that the isomerization rate should be less than 3×10^6 sec^{-1}. This means that the TST overestimates the isomerization rate by at least 3 orders of magnitude.

Because the collision rates are firm upper limits to the cooling rates, it must be the calculated isomerization rates that are in error. While an order of magnitude discrepancy could perhaps be accommodated with appropriate adjustments of the activation energies and vibrational frequencies of the transition state, the 2 to 3 orders of magnitude difference cannot be reconciled. We thus reach the inescapable conclusion that the isomerization rates for these molecules are orders of magnitude smaller than predicted by the RRKM (or TST) theory.

How reasonable is it that the statistical theory should break down for molecules as large as these cyclic ketones? The statistical theory has been validated so often that its proposed breakdown must be viewed with considerable caution. The breakdown of TST does not appear to result from the low density of states. The density of states of vibrational states alone in 3-ethylcyclohexanone at an energy of 5 kcal/mol is approximately 550 states/cm^{-1}. When two degrees of rotations ($B = 1$ cm^{-1}) are included, this jumps to over 10^5 states/cm^{-1}. This can be compared to the vibrational density of states of NO_2 or H_2CO at their respective dissociation limits, which have been determined to be 0.3 states/cm^{-1} [33,34] and 400 states/cm^{-1},[35] respectively. These molecules were cooled in a molecular beam so that rotations play a far less important role than in our thermal sample. Yet, these small molecules decay with rates that are well accounted for by statistical theories. A recent theoretical analysis[37] of the NO_2 dissociation on a three-dimensional global potential energy surface of the ground state showed that the internal modes are totally mixed near the dissociation limit so that IVR is complete in less than a picosecond, and the rate constants derived from this study (using the statistical adiabatic channel model,[36] RRKM theory, and classical trajectory calculations reactions[1]) agree quite well with the measured rate constants. We thus conclude that a high density of states is not the only nor perhaps even the key ingredient for statistical behavior.

We suggest here that the origin of the nonstatistical rate constants is a result of two factors, namely the low activation energy and the large number of vibrational modes. The essential feature required for the statistical theory is that the vibrational modes are coupled sufficiently to permit energy flow among them. Coupling of vibrational states increases with the energy because potential energy for a vibrational mode is most harmonic at low energies and becomes increasingly anharmonic with increasing energy. In the case of NO_2 and H_2CO, the vibrational energy per oscillator at the energy of the transition state is 8400 and 4700 cm^{-1}, respectively. This can be compared to just 30 cm^{-1} per oscillator for the case of ethyl cyclohexanone. This calculation assumes a barrier height of 1500 cm^{-1} and an equal distribution of energy among the 48 oscillators with frequencies below 1500 cm^{-1}. If we take into account the fact that the low frequencies have a higher energy content, then the lowest four frequencies of 55, 75, 157, and 174 cm^{-1} contain an average energy of 175, 165, 131, and 125 cm^{-1}, respectively. The energy content of the higher modes decreases progressively. It is apparent that most of the oscillators are in their ground states during the course of the reaction.

In recent years, evidence of such nonstatistical behavior in low barrier isomerization reactions has been building. Borchardt and Bauer[38] have investigated the isomerization of aziridine by gas-phase NMR spectroscopy. They found the rates to be much slower than predicted by RRKM. More recently, Leitner and Wolynes[7] investigated the classic trans-cis stilbene reaction theoretically. They concluded that “in large molecules with low isomerization barriers, few vibrational modes need be excited at energies sufficient to allow reaction. Quantum effects on intramolecular energy flow are thus especially important.” They were able to reproduce the experimental rates using their local random matrix theory, which takes into account the limited IVR in these low energy reactions. The previously mentioned isomerization in 2-fluoroethanol[9] is another example of a reaction inhibited by slow IVR.

Of major interest is the fact that the reaction, which is nonstatistical in the gas phase, appears to become statistical in solution phase. The fact that Anet et al.[26] were able to use TST to determine a barrier of 4 kcal/mol implies that the reaction is near statistical in the condensed phase. That is, if the reaction rate had been much slower than statistical, either the entropy or the enthalpy of reaction would have deviated greatly from the expected values. The statistical reaction in solution even at low temperatures suggests that energy flow in solution is aided by solvent−solute interactions. The numerous collisions between the solvent and the molecule not only maintain the reaction in the high-pressure limit, but they also aid IVR. A recent study by Leitner[10] of isomerization rates in various density fluids suggests that the rate is much closer to the TST limit in the liquid phase, but that even in that limit the rate is lower than TST by a factor of about 3.

The other interesting aspect of the rates is that the ethyl rotor reaction is much faster than the axial−equatorial interconversion rate, even though they have nearly the same activation energies and entropies. In some way, IVR is not as important in the ethyl rotor motion as it is in the axial−equatorial interconversion.

Let us consider now the empirical finding of Ruoff et al.[18] who noted that molecules with conformational barriers in excess of 1 kcal/mol tend to freeze out the higher energy as well as the lower energy isomer during molecular beam expansions. This is a rather remarkable finding. If we assume a moderately negative entropy of activation of −6 cal/mol-K and a barrier height of 1 kcal/mol, the TST rate constant at room temperature is 6×10^{12} sec^{-1}. This rate is 3 orders of magnitude higher than the collision rate of 6×10^9 sec^{-1} at one atmosphere pressure at room temperature. We can conclude that all of these low barrier isomerization reactions proceed with rates that are orders of magnitude slower than predicted by TST.

This analysis of the relative isomerization and collisional deactivation rates has been based solely on the initial rates during the initial stage of expansion. A proper treatment of the whole process should be carried out with the aid of the master equation,[2,39,40] which takes into account the forward and backward isomerization steps as well as the collisional activation and deactivation steps during the whole expansion (drop in gas density and temperature). Such a treatment was attempted, and the results confirmed the more qualitative conclusions drawn here. But, because of the many approximations necessary to fit the data, a firm quantitative basis for data analysis was lacking. As a result, this attempt at a master equation analysis is not included in this paper.

Acknowledgment. We thank the National Science Foundation and the North Carolina Supercomputing Center (NCSC) for support of this work. We are also grateful to David Leitner for helpful discussions. Finally, we thank Wing Tsang of NIST for many helpful discussions and for carrying out some preliminary master equation calculations that gave us the courage to reach our conclusions.

References and Notes

(1) Baer, T.; Hase, W. L.*Unimolecular Reaction Dynamics: Theory and Experiments*; Oxford University Press: New York, 1996;

(2) Holbrook, K. A.; Pilling, M. J.; Robertson, S. H.*Unimolecular Reactions*; John Wiley & Sons: Chichester, 1996.

(3) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Chem. Phys.* **1971**, *54*, 2275−2276.

(4) Block, P. A.; Jucks, K. W.; Pedersen, L. G.; Miller, R. E. *Chem. Phys.* **1989**, *139*, 15−30.

(5) Huang, Z. S.; Jucks, K. W.; Miller, R. E. *J. Chem. Phys.* **1986**, *85*, 3338−3341.

(6) Baskin, J. S.; Banares, L.; Pedersen, S.; Zewail, A. H. *J. Phys. Chem.* **1996**, *100*, 11920−11933.

(7) Leitner, D. M.; Wolynes, P. G. *Chem. Phys. Lett.* **1997**, *280*, 411−418.

(8) Leitner, D. M.; Wolynes, P. G. *J. Phys. Chem. A* **1997**, *101*, 541−548.

(9) McWhorter, D. A.; Hudspeth, E.; Pate, B. H. *J. Chem. Phys.* **1999**, *110*, 2000−2009.

(10) Leitner, D. M. *Int. J. Quantum Chem.* **1999**, *75*, 523−531.

(11) Borchardt, D. B.; Bauer, S. H. *J. Chem. Phys.* **1986**, *85*, 4980−4988.

(12) Dayton, D. C.; Pedersen, L. G.; Miller, R. E. *J. Phys. Chem.* **1992**, *96*, 1087−1095.

(13) Klots, T. D.; Ruoff, R. S.; Gutowsky, H. S. *J. Chem. Phys.* **1989**, *90*, 4217−4221.

(14) Bernstein, E. R.; Im, H. S.; Young, M. A.; Secor, H. V.; Bassfield, R. L.; Seeman, J. I. *J. Org. Chem.* **1991**, *56*, 6059−6063.

(15) Felder, P.; Gunthard, Hs. H. *Chem. Phys.* **1982**, *71*, 9−25.

(16) Cornish, T. J.; Baer, T. *J. Phys. Chem.* **1990**, *94*, 2852−2857.

(17) Cable, J. R.; Tubergen, M. J.; Levy, D. H. *Faraday Discuss. Chem. Soc.* **1988**, *86*, 143−152.

(18) Ruoff, R. S.; Klots, T. D.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys.* **1990**, *93*, 3142−3150.

(19) Potts, A. R.; Baer, T. *J. Phys. Chem. A* **1997**, *101*, 8970−8978.

(20) Potts, A. R.; Baer, T. *J. Chem. Phys.* **1998**, *108*, 869−875.

(21) Potts, A. R.; Baer, T. *J. Chem. Phys.* **1996**, *105*, 7605−7612.

(22) Nesselrodt, D. R.; Potts, A. R.; Baer, T. *J. Phys. Chem.* **1995**, *99*, 4458−4465.

(23) Kim, D.; Baer, T. *J. Phys. Chem. A* **2000**, *104*, 509−513.

(24) Kim, D.; Baer, T. *Chem. Phys.* **2000**, *256*, 251−258.

(25) Schwartz, R. N.; Slawsky, Z. I.; Herzfeld, K. F. *J. Chem. Phys.* **1952**, *20*, 1591.

(26) Anet, F. A. L.; Chmurny, G. N.; Krane, J. *J. Am. Chem. Soc.* **1973**, *95*, 4423−4424.

(27) Wiberg, K. B.; Murcko, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 8029−8038.

(28) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.

(29) Weston, R. E.; Flynn, G. W. *Annu. Rev. Phys. Chem.* **1992**, *43*, 559−589.

(30) Michaels, C. A.; Mullin, A. S.; Flynn, G. W. *J. Chem. Phys.* **1995**, *102*, 6682−6695.

(31) Cottrell, T. L.; McCoubrey, J. C. *Molecular Energy Transfer in Gases*; Butterworth: London, 1961.

(32) Miller, D. R. In *Atomic and Molecular Beam Methods*; Scoles, G., Ed.; Oxford University Press: New York, 1988; pp 14−53.

(33) Brucker, G. A.; Ionov, S. I.; Chen, Y.; Wittig, C. *Chem. Phys. Lett.* **1992**, *194*, 301−308.

(34) Miyawaki, J.; Yamanouchi, K.; Tsuchiya, S. *J. Chem. Phys.* **1993**, *99*, 254−264.

(35) Polik, W. F.; Guyer, D. R.; Moore, C. B. *J. Chem. Phys.* **1990**, *92*, 3453−3470.

(36) Quack, M.; Troe, J. *Ber. Bunsen-Ges. Phys. Chem.* **1974**, *78*, 240−252.

(37) Grebenshchikov, S. Yu.; Beck, C.; Flöthman, H.; Schinke, R.; Kato, S. *J. Chem. Phys.* **1999**, *111*, 619−632.

(38) Bauer, S. H.; Borchardt, D. B.; Chiu, N.-S. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 407−412.

(39) Green, N. J. B.; Marchant, P. J.; Perona, M. J.; Pilling, M. J.; Robertson, S. H. *J. Chem. Phys.* **1992**, *96*, 5896−5907.

(40) Tsang, W.; Bedanov, V. M.; Zachariah, M. R. *J. Phys. Chem.* **1996**, *100*, 4011−4018.