specific second-order rate constant for the slower exchange reaction. This was necessitated by a slight ambiguity in the data reported in ref 6g.

(12) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 2371 (1972).

(13) (a) Program PSI/77 by W. L. Jorgensen. Program No. 340, available from QCPE, Department of Chemistry, Indiana University, Bloomington, Ind. 47405. (b) The wave functions used for the Jorgensen plot were obtained from extended Hückel calculations. This was necessitated by program limitations. Qualitatively, the wave functions are the same calculated by EHT or by ab initio methods at either the STO-3G or 4-31G levels. We thank Mr. D. Grier and Dr. B. E. R. Schilling for their assistance in obtaining the EHT calculations and the Jorgensen plots.

(14) N. D. Epiotis, R. L. Yates, F. Bernardi, and S. Wolfe, *J. Am. Chem. Soc.*, **98**, 5435 (1976).

(15) See ref 4d, footnote 18.

(16) To facilitate comparison with Fava's work, we report here the Mulliken population analysis at the STO-3G level. The 4-31G results are qualitatively similar.

(17) See ref 3b, p 36, and references cited therein.

(18) An alternative explanation for the diminution of the V_1 term is that at the transition state for deprotonation the carbon is planar. In such a case V_1 must be zero owing to the symmetry of the system. Other experimental data[7b] indicates this not to be the case.

(19) E. L. Eliel and R. L. Willer, *J. Am. Chem. Soc.*, **99**, 1936 (1977).

(20) O. Hofer and E. L. Eliel, *J. Am. Chem. Soc.*, **95**, 8045 (1973).

(21) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1965, p 28.

(22) Similar results regarding determination of dihedral angles are obtained by application of programs such as Allinger's MMI force field.[23] Using our current parametrization of this program for sulfonium cations (see ref 7b) the relevant dihedral angles obtained for **9a** are H_c, 173°; H_t, 55°; **9b**, H_c, 66°; H_t, 50°.

(23) See N. L. Allinger and D. Y. Chung, *J. Am. Chem. Soc.*, **98**, 6798 (1976), and previous papers in this series.

Transition State Vibrational Analysis for the Methyl Isocyanide Rearrangement, $CH_3NC \rightarrow CH_3CN$

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Abstract: The title reaction is perhaps the most exhaustively studied of all unimolecular reactions to be examined by the experimental methods of modern chemical kinetics. Previous theoretical work on this and the related $HNC \rightarrow HCN$ reaction appears to demonstrate that the $CH_3NC \rightarrow CH_3CN$ potential energy surface is qualitatively described within the Hartree-Fock approximation. In the present ab initio self-consistent-field study, a double ζ plus polarization basis set, described as C(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p), N(9s 5p 1d/4s 2p 1d), was employed. The transition state or saddle point for the CH_3NC rearrangement was precisely located using gradient techiques. The same methods were used to evaluate the harmonic vibrational frequencies about the transition state or activated complex. Although the transition-state structure is quite different from that suggested by Schneider and Rabinovitch, the present theoretical vibrational frequencies are in surprisingly good agreement with those deduced from experiment via the RRKM hypothesis. Using the ab initio rotational and vibrational parameters in conjunction with activated-complex theory yields experimental rate constants about 50% greater than experiment.

Introduction

The Rice-Ramsperger-Kassel-Marcus (RRKM) theory is one of the pillars of modern chemical kinetics.[1,2] The chief merits of RRKM, of course, are its simplicity and typical order-of-magnitude correctness. Furthermore, over the years the method has proven quite adaptable to the incorporation of quantum effects and other refinements.[3] The most obvious criticism of RRKM theory as it is widely used is that it contains a number of empirically adjustable parameters, namely, the transition state vibrational frequencies and moments of inertia. These are sometimes empirically deduced from the experimental rate constants. Since transition state vibrational frequencies cannot be measured experimentally, it has been somewhat difficult to assess the absolute validity of RRKM.

Probably the most exhaustive examination of the RRKM theory has been carried out by Rabinovitch and co-workers[4-7] for the methyl isocyanide isomerization

$$CH_3NC \rightarrow CH_3CN \qquad (1)$$

In this respect the correspondence between Bunker and Rabinovitch[8-11] concerning whether or not CH_3NC is an "RRKM molecule" is of special interest. Schneider and Rabinovitch[4] have assigned transition state vibrational frequencies for (1), but they conclude that the twisting vibration is a significant and arbitrary frequency. Moreover, different values for the other frequencies are clearly possible. If reliable values of all frequencies could be determined theoretically, an immediate assessment of the RRKM method would be possible.

Several other experimental studies of the CH_3NC isomerization have also been reported, including thermal,[12] photochemical,[13] hot atom chemistry,[14] and most recently laser spectroscopic studies.[15-17] For example, in their recent laser study Reddy and Berry[15] were able to photoisomerize CH_3NC by directly pumping the fourth overtone of the CH stretch. Even more recently Guillory and co-workers[17] observed (among products other than CH_3CN) CN, CH, and C_2 from their infrared multiphoton photolysis of CH_3NC. However, they concluded that the isomerization of CH_3NC occurs quantitatively at energies just above threshold, and other products result from the secondary photolysis of CH_3CN. With this number and variety of experimental studies, it is no wonder that the methyl isocyanide rearrangement has been the target of several theoretical investigations.

Theoretical Background and Present Approach

At least five distinct theoretical studies of the methyl isocyanide rearrangement have been reported, ranging from extended Hückel[18] to MINDO[19] to ab initio studies.[20-22] Interestingly, none of the ab initio studies has precisely determined the transition-state geometry in the manner possible using modern gradient techniques.[23] However, the self-consistent-field (SCF) transition state of Liskow, Bender, and Schaefer (LBS),[20] obtained from a double ζ (DZ) basis set, should be quite close to the true DZ SCF saddle point. An in-

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Table I. Cartesian Coordinates (Bohr Radii) of the Transition State for the $CH_3NC \rightarrow CH_3CN$ Isomerization

	x	y	z
H_1	−3.878 619 5	1.909 588 7	0.0
H_{2a}	−3.971 796 4	−0.984 584 7	1.696 048 3
H_{2b}	−3.971 796 4	−0.984 584 7	−1.696 048 3
C_{Me}	−3.341 742 0	−0.054 905 8	0.0
N	−0.004 597 1	1.258 436 6	0.0
C	−0.180 265 0	−0.960 451 7	0.0

teresting finding of LBS was that their predicted barrier height of 60.4 kcal was notably greater than the experimental activation energy of Schneider and Rabinovitch,[4] namely, 38.4 kcal.

This activation-energy discrepancy was resolved when a more detailed theoretical examination of the prototype

$$HNC \rightarrow HCN \qquad (2)$$

reaction appeared.[24] There Pearson, Schaefer, and Wahlgren (PSW)[24] properly determined the transition state and found that polarization basis functions (d functions on C and N, p functions on H) lower the predicted barrier decidedly. In addition PSW predicted a 4.0-kcal difference between the classical barrier height (34.9 kcal) and the activation energy (30.9 kcal) (in the sense of transition-state theory[25]), since the transition-state zero-point vibrational energy is less than the zero-point energy of the reactant HNC. Electron correlation has a relatively small (compared, for example, to potential energy surfaces like $F + H_2$)[26] effect on the $HNC \rightarrow HCN$ potential surface, lowering the predicted barrier by 5 kcal.

Quite recently Redmon, Purvis, and Bartlett (RPB)[22] reported a direct investigation of the effects of basis set and electron correlation for CH_3NC, the transition state of LBS, and CH_3CN. At the SCF level they found the classical barrier height reduced from 60.4 (DZ basis set) to 48.1 kcal (DZ + P basis). A rather complete description of correlation effects using many-body perturbation theory lowered the barrier an additional 2.8 kcal to 45.3 kcal. When the PSW expectation that the transition state should have significantly less zero-point energy than CH_3NC is considered, the agreement with the experimental activation energy of 38.4 kcal is quite satisfactory.

The present study begins with the finding of Redmon, Purvis, and Bartlett that the DZ + P basis set, self-consistent-field level of theory provides a qualitatively correct description of the $CH_3NC \rightarrow CH_3CN$ potential energy surface. First the transition state was precisely determined at the DZ + P SCF level using analytic gradient techniques.[23] We then used the same techniques to obtain quadratic force constants and harmonic vibrational frequencies[27] about the transition state. These along with the saddle-point moments of inertia have been subsequently employed in an RRKM analysis[1,2] of the reaction. Since both the vibrational frequencies and moments of inertia should be reliably predicted with these theoretical methods, a meaningful evaluation of the RRKM method should now be possible.

The Potential Energy Surface

The precise double ζ plus polarization (DZ + P) basis set used here is that advocated by Dunning,[28] and based on Huzinaga's sp primitive Gaussian basis set.[29] This basis may be described as C(9s 5p 1d/4s 2p 1d), H(4s 1p/2s 1p), N(9s 5p 1d/4s 2p 1d). The carbon and nitrogen d function Gaussian exponents were $\alpha = 0.75$ and 0.80, respectively. All six d-like functions, including the $(x^2 + y^2 + z^2) = 3s$ function, were used here, resulting in a total of 63 contracted Gaussian functions. As discussed by Pulay,[30] the d functions were constructed as linear combinations of p functions. However, a calculation at the transition state thus obtained, but with conventional Cartesian primitives (e.g., $xye^{-\alpha r^2}$), yielded an energy differing by only 0.000 114 hartree from the present Pulay result. The scale factor on the hydrogen s functions was $\zeta = 1.2$ and the hydrogen p exponent was 1.0.

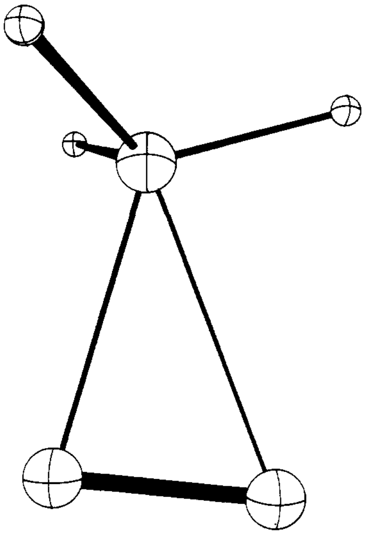

Figure 1. Transition-state geometry for the $CH_3NC \rightarrow CH_3CN$ isomerization.

Table II. Comparison of Theoretical and Experimental Equilibrium Geometries for HNC and HCN[a]

		theory	expt[b]
HNC	$r_e(HN)$	0.986	0.9940 ± 0.0008
	$r_e(NC)$	1.159	1.1689 ± 0.0002
HCN	$r_e(HC)$	1.062	1.0655
	$r_e(CN)$	1.137	1.1532

[a] The theoretical methods used involve precisely the approach (DZ + P SCF) employed to determine the $CH_3NC \rightarrow CH_3CN$ transition state here. Bond distances are given in Å. [b] Experimental HNC r_e structure is from R. A. Creswell and A. G. Robiette, *Mol. Phys.*, 36, 869 (1978). Experimental HCN r_e structure is from G. Winnewisser, A. G. Maki, and D. R. Johnson, *J. Mol. Spectrosc.*, 39, 149 (1971).

The $CH_3NC \rightarrow CH_3CN$ transition state is seen in Figure 1 and the Cartesian coordinates of each atom are given in Table I. The latter should be a great help in avoiding confusion should this transition state be used in future theoretical studies.

Before discussing the transition-state geometry seen in Figure 1, it is well to have some idea of the reliability of structural predictions at this level of theory.[31,32] To this end we compare in Table II the theoretical structures of HNC and HCN (predicted in precisely the same manner as the CH_3NC transition state reported here) with the experimental equilibrium geometries. As expected[31,32] the agreement between theory and experiment is good, the bond-distance differences being 0.008 (H-N), 0.010 (N-C), 0.004 (HC), and 0.016 Å (C-N). From this and related comparisons, we expect the $CH_3NC \rightarrow CH_3CN$ transition state bond distances to be reliable within ±0.03 Å.

The first comparison to be made is between Figure 1 and the DZ SCF approximate transition state of LBS. This comparison is made in Table III. It should first be noted that LBS inadvertently reported a value of 100.8° for θ, the angle between the cyanide carbon, the center of mass of the CN group, and the methyl carbon. In fact, for the coordinate system defined in their Figure 1, 100.8° is not θ but its complement (180° − θ). In other words, the correct value of θ is 79.2°, implying that the transition state is closer to the product CH_3CN than to the reactant CH_3NC. Here the DZ + P SCF transition state also

Table III. Comparison of Transition State Geometrical Parameters for the CH_3NC Isometization[d]

parameter	CH_3NC[a]	Schneider-Rabinovitch	Liskow	DZ + P SCF present work
r(CH)	1.090_5	1.094	1.074	1.0777 1.0764 1.0764
r(CC)	2.589_5	1.94[b] or 1.64[c]	1.815	1.7403
r(CN)	1.418_9	1.61	2.001	1.8978
r(N≡C)	1.170_6	1.20	1.198	1.1779
ϕ(HCH)	109.6_0°	109.8°	112.5°	112.98° 111.05° 111.05°

[a] L. Halonen and I. M. Mills, *J. Mol. Spectrosc.*, **73**, 494 (1978). This is an experimental r_s structure. [b] This CC distance corresponds to the Schneider-Rabinovitch 300 model. [c] This CC distance corresponds to the Schneider-Rabinovitch 600 model. [d] Bond distances are given in Å.

lies closer to product than reactant. Furthermore, the same qualitative result is found for the HNC → HCN isomerization. Thus both of these transition states violate Hammond's postulate,[34] which states that for an exothermic reaction (such as the CH_3NC and HNC rearrangements) the transition state should resemble the reactant geometry.

The actual transition state bond distances are noticeably shorter than those obtained by LBS with their smaller basis set. However, the two structures are otherwise qualitatively similar. A key assumption in the LBS work was that the methyl group maintains C_{3v} local symmetry at the transition state. The present complete geometrical optimization shows that this assumption is a reasonable one. Table III reveals that the transition state in fact contains a plane of symmetry with two C-H distances being 1.0764 Å and the third 0.0013 Å longer. Similarly, two of the HCH angles are 111.05° and the third 1.93° larger. The transition state hydrogen atom which lies in the plane of the three heavy atoms lies closer to the N than the C end of the cyano group. That is, this hydrogen is eclipsed to the nitrogen atom. This is not surprising, since the eclipsing of one of the hydrogens to the cyano C atom should lead to a much stronger (shorter distance) repulsive interaction. The same conformation was found to lie lowest by LBS when the methyl C_3 axis was constrained to be perpendicular to the cyano N-C internuclear axis.

The second pertinent comparison is between the present theoretical transition state geometry and the two models proposed by Schneider and Rabinovitch. As mentioned above, their assumption of local C_{3v} symmetry for the CH_3 group turns out to be quite reasonable. Also their suggestion that the cyano N-C distance differs only slightly from that in the CH_3NC molecule has been placed on a sound theoretical foundation. However, the Schneider-Rabinovitch (SR) transition state C_{Me}-N and C_{Me}-C distance differ significantly from those predicted here. For both the SR 300 and 600 models, the C_{Me}-N distance of 1.61 Å is 0.29 Å less than the DZ + P SCF value. With the 300 and 600 models, respectively, C_{Me}-C distances 0.20 Å greater and 0.10 Å smaller than the theoretical value are in evidence in Table III.

Finally, a structural comparison between the transition state and the reactant molecule CH_3NC is in order. We see first that the transition state C-H distances are shortened somewhat relative to those for the reactant. This same qualitative result was found by LBS and can perhaps be attributed to the fact that these three atoms are much further from the N atom than in CH_3NC. As seen in Table II, the N≡C distances predicted at the DZ + P SCF level of theory are expected to be too short, by perhaps 0.013 Å. If this correlation were reliable, the true transition state N≡C distance should be 1.191 Å, which is 0.02 Å longer than that known experimentally for CH_3NC. It seems apparent, then, that the CN triple bond is essentially maintained along the reaction pathway of lowest energy. A last point to be made is that there is some tendency of the methyl group toward planarity along the minimum-energy path. That is, the HCH angles open slightly from 109.6° for CH_3NC to 111-113° at the saddle point. However, this opening is much less than suspected by Van Dine and Hoffmann[18] on the basis of their extended Hückel studies.

Table IV. Moments of Inertia (amu Å^2) for CH_3NC and the Transition State for Its Isomerization to CH_3CN

	exptl CH_3NC	Schneider-Rabinovitch transition state 600 model	Schneider-Rabinovitch transition state 300 model	Bunker-Hase	DZ + P SCF transition state
I_A	3.20	12.53	11.59	11.89	11.80
I_B	50.12	25.77	31.65	43.62	32.87
I_C	50.12	35.08	40.01	52.30	41.42
internal ratio I_r		3.53	4.02	5.51	4.24

Transition State Rotational and Vibrational Analyses

The parameters which characterize the transition state in the RRKM theory are the moments of inertia and vibrational frequencies. Our predictions of these parameters are seen in Tables IV and V, which form the basis of the present section's discussion.

Moments of inertia compared in Table IV are the experimental CH_3NC values, those for two of the SR models[4] of the transition state, those given by Bunker and Hase[10] in their RRKM treatment, and finally the present DZ + P SCF values. All four sets of transition-state moments of inertia concur that the smallest moment of inertia I_A is much increased relative to its value for CH_3NC. Except for the Bunker-Hase (BH) I_c value, there is concurrence that the saddle-point values of I_B and I_C are reduced relative to those for the symmetric top CH_3NC. In general the BH moments of inertia are in poorest agreement with the ab initio predictions. The SR 300 values are in very good agreement with the theoretical predictions, but Table III shows that this is purely fortuitous. Namely, the SR 300 model has a C_{Me}-C distance 0.20 Å too long and a C_{Me}-N distance 0.29 Å too short, but these two discrepancies nearly cancel, giving very reasonable moments of inertia.

The quantity appearing in the RRKM expression for k_∞, the high pressure limit rate constant, is the internal ratio I_r

$$I_r = \frac{\sigma}{\sigma^\dagger}\left(\frac{I_A{}^\dagger I_B{}^\dagger I_C{}^\dagger}{I_A I_B I_C}\right)^{1/2} \qquad (3)$$

where the daggers denote transition-state properties. For CH_3NC the symmetry number σ is 3, while for the transition state $\sigma^\dagger = 1$. These internal ratios have been calculated for the four transition states and the results are compared in Table IV. As expected from the moments of inertia, the BH model yields the poorest agreement with the DZ + P SCF results, while the SR 300 model is in fortuitously good agreement. It has often been remarked that the RRKM theory is *insensitive* to the chosen reaction coordinate and to moderate variations in the structure and frequencies of the activated complex provided that these give adequate correspondence with the experimental high-pressure frequency factor. It is worth noting here that substituting the BH moments of inertia for the SR 600 values increases the rate constants by no less than 56%. Since both the BH and SR transition states were arrived at by "masters of the art" and are equally plausible, the need for more rigorous transition-state determinations is apparent.

Harmonic vibrational frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix. Two values are given for each theoretical vibrational frequency

Table V. Vibrational Frequencies (cm^{-1}) for CH_3NC and the Transition State for Its Isomerization to CH_3CN

CH_3NC type	CH_3NC^a	Schneider-Rabinovitch transition state	Bunker-Hase transition state	DZ + P SCF theory transition state
C—H stretch	3014	2998	3039	3411 (3070)
C—H stretch	3014	2998	3039	3388 (3049)
C—H stretch	2966	2998	2925	3272 (2945)
N≡C stretch	2166	1990	2190	2189 (1970)
CH_3 deformation	1467	1443	1388	1599 (1439)
CH_3 deformation	1467	1443	1342	1590 (1431)
CH_3 deformation	1429	1443	1342	1457 (1311)
CH_3 rocking	1129	1041	941	1083 (975)
CH_3 rocking	1129	1041	941	1063 (957)
C—N stretch	945	600	870	677 (609)
C—N≡C bend	263	270 or 560	twist free rotor	255 (230)
C—N≡C bend	263			458*i* (412*i*)

[a] T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", *Nat. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 1 (1972).

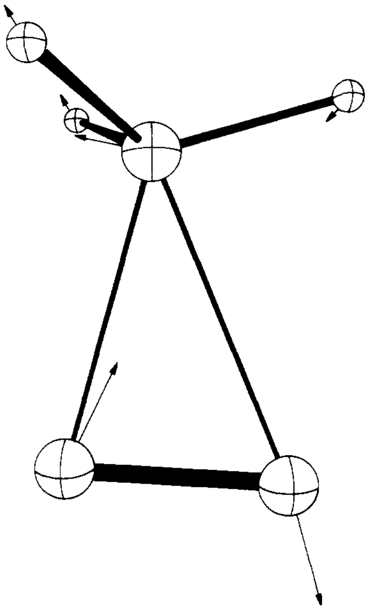

Figure 2. Reaction coordinate, i.e., normal mode of imaginary frequency, for the methyl isocyanide rearrangement.

in Table V. The first is the ab initio DZ + P SCF harmonic result and the second value (in parentheses) is 90% of the first. Experience suggests that this is a reasonable correction factor for electron correlation and anharmonicity effects.[23,25] A specific example obtained by precisely the DZ + P SCF method used here is the vibrational frequencies of HCN,[33] predicted to be 3636, 2404, and 858 cm^{-1}. These results are respectively 110, 115, and 120% of the known experimental values.[36]

For the most part the predicted transition state vibrational frequencies are consistent with the empirical suggestions of SR and BH. Of course all degeneracies among vibrational frequencies are removed, since the transition state has only a plane of symmetry. For example, the C-H stretching modes are split by 21 cm^{-1}. Similarly, the CH_3 deformations are split by only 8 cm^{-1}, and the CH_3 rocking modes by 18 cm^{-1}. Among the modes for which SR and BH differ significantly, first is the C-N stretch. Our prediction of 609 cm^{-1} is much closer to the SR value of 600 cm^{-1} than to BH's 870 cm^{-1}. The most controversial vibrational degree of freedom is the methyl rotation of the CH_3 group. Assuming this degree of freedom to be harmonic, theory predicts values of 255 (uncorrected) and 230 cm^{-1} (corrected). Both values are in very good agreement with the SR 300 model value of 270 cm^{-1}. However, this portion of the potential-energy surface is not in fact very harmonic and we will return to this point later.

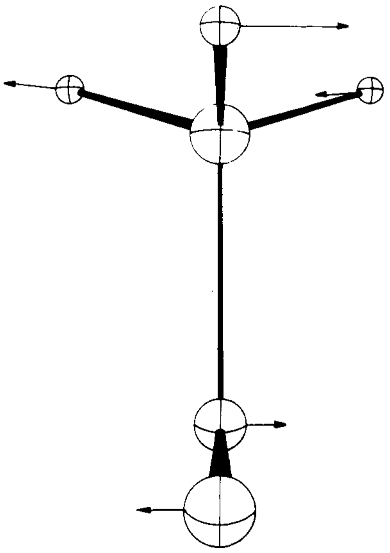

Figure 3. The normal mode of lowest real vibrational frequency for the methyl isocyanide isomerization.

Inasmuch as transition state vibrational analysis cannot be obtained from experiment, it is important to establish the nature of the controversial normal modes. The reaction coordinate ($\nu = 458i$ or $412i$ cm^{-1}) is illustrated in Figure 2. There is seen the precise character of motion along the minimum-energy path at the saddle point. Among the real vibrational frequencies, the methyl "rotation" is seen in Figure 3, where it is apparent that relatively small displacements of the three heavy atoms are involved. Finally in Figure 4 is displayed the other low-frequency mode, that with $\nu = 677$ (609) cm^{-1}. This normal mode is a C-N stretch for the isolated reactant CH_3NC molecule. Figure 4 shows clearly that for the transition state the 677-cm^{-1} vibration represents a breathing motion for the CCN three-membered ring. The fact that this is such a low frequency is due to the long (relative to normal chemical bonds) C-C (1.74 Å) and CN (1.90 Å) distances at the saddle point.

The DZ + P SCF energies obtained here at the two stationary points were −131.920 03 (CH_3NC) and −131.847 56 hartrees (transition state). The difference is the predicted classical barrier height, 45.5 kcal/mol. However, comparison with the experimental activation energy requires at the least that zero-point energies be taken into account. Making the harmonic assumption

$$E(\text{zero-point energy}) = \tfrac{1}{2}\sum_i \nu_i \qquad (4)$$

the zero-point energy is approximated as 27.5 kcal/mol. Estimating the transition-state zero-point vibrational energy is

Table VI. Summary of ab Initio RRKM Results for the $CH_3NC \rightarrow CH_3CN$ Isomerization[a]

inactive rotation			active rotation		
total energy, kcal	vibrational energy, kcal	harmonic rate constant, s^{-1}	total energy, kcal	vibrational energy, kcal	harmonic rate constant, s^{-1}
40	2.3	3.3×10^{8}	40.3	2.4	3.2×10^{8}
50	12.3	1.1×10^{10}	50.3	12.4	1.3×10^{10}
60	22.3	5.7×10^{10}	60.3	22.4	7.6×10^{11}
70	32.3	1.7×10^{11}	70.3	32.4	2.4×10^{11}
80	42.3	3.7×10^{11}	80.3	42.4	5.5×10^{11}
90	52.3	6.8×10^{11}	90.3	52.4	1.0×10^{12}

[a] With the external rotation along the C—N≡C active, 0.3 kcal of the total energy is the energy of the active rotation.

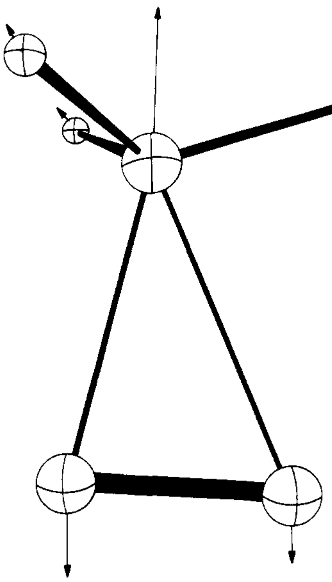

Figure 4. The $CH_3NC \rightarrow CH_3CN$ transition state vibrational frequency which corresponds to the 945-cm^{-1} C-N stretch of the reactant molecule. The actual value of this transition-state frequency is 677 cm^{-1}.

more difficult, but, if the vibrational frequencies in parentheses are used, one obtains 25.7 kcal. This suggests that the activation energy should be 1.8 kcal less than the classical barrier, or 43.7 kcal. If we further accept the prediction of Redmon, Purvis, and Bartlett[22] that the transition state has 2.8 kcal more correlation than CH_3NC, a final theoretical estimate for the activation energy of 40.9 kcal may be made. This estimate is in very satisfactory agreement with the SR experimental vlaue, 38.4 kcal, which corresponds to an E_0 of 37.85 kcal in the 300 model.

Activated Complex and RRKM Theory Results

The dynamical calculations reported in this section were very generously carried out by Professor William L. Hase of Wayne State University, Detroit, Mich. Transition state vibrational frequencies used were those in parentheses in Table V. Activated complex results were obtained at 400, 500, and 600 K, with the barrier E_0 chosen to give the experimental activation energy (38.4 kcal) at 500 K. At the three chosen temperatures, the activation energies E_a were 38.3, 38.4 (to fit experiment), and 38.5 kcal/mol. The analogous values of the preexponential factors A (s^{-1}) were 5.33×10^{13}, 6.13×10^{13}, and 6.80×10^{13}. For comparison the experimental value at 500 K is $10^{13.6} = 4 \times 10^{13}$, or about 65% of our ab initio activated complex result. This might be a significant difference, possibly suggesting some non-RRKM behavior in the thermal experiments. However, considering the approximations[1-3] inherent in activated-complex theory, the agreement is encouraging. This is especially true when one realizes that there are *no* adjustable parameters in the present implementation of the theory.

Some comment should be made regarding the sensitivity of the activated-complex results to the ab initio harmonic vibrational frequencies. The vibrational partition function, of course, is most strongly affected by low-frequency normal modes. For example, at 500 K the lowest frequency theoretical mode, 230 cm^{-1}, contributes a factor of 2.065 to the partition function. Increasing this frequency to 255 cm^{-1}, the unscaled ab initio value in Table V, decreases the partition function factor to 1.923 or 93% of the 230-cm^{-1} value. The latter partition function reduces the activated complex rate constant to 5.7×10^{13} s^{-1}, in better agreement with experiment, 4×10^{13} s^{-1}. Nevertheless it appears that theoretically justifiable adjustments of the vibrational frequencies will still leave an activated complex theory rate constant somewhat greater than the experimental rate constant of Schneider and Rabinovitch.[4]

The RRKM results refer to CH_3NC thermally rotationally excited (300 K), with the vibrational energy being varied. Hase carried out two different types of calculations, the first with the external rotation along the C—N≡C axis inactive (case I) and the second with this external rotation active (case II). Both calculations used harmonic state counting and are summarized in Table VI.

The "Difficult" Degree of Freedom

Here we return to the treatment of the transition state vibrational degree of freedom. The frequency 255 (230) cm^{-1} was obtained by diagonalizing the 18×18 matrix of mass-weighted Cartesian force constants. However, a more realistic treatment should recognize that this degree of freedom is highly anharmonic. LBS suggested[20] a threefold barrier for methyl rotation, with height ~1 kcal.

The question of primary interest at present is the relationship between the partition function resulting from the proper treatment of this threefold barrier and the partition function (value 2.065 cited above) arising from the RRKM harmonic oscillator treatment with $\nu = 230$ cm^{-1}. One intuitively suspects that, inasmuch as rotational partition functions are usually greater than vibrational partition functions,[37] the more nearly correct treatment of this degree of freedom as an internal rotation should increase the simple harmonic oscillator partition function.

A more specific assessment of the problem may be made by noting its similarity to the ethane internal rotation problem. For ethane detailed partition function calculations as a function of the barrier height are reported in Table 141 of Herzberg's volume[38] on infrared and Raman spectra. For the experimental internal rotation barrier $V_0 = 2.93$ kcal,[39] Herzberg's table may be interpolated to yield a partition function of 1.93. Using the experimental vibrational frequency[39] of 289 cm^{-1} for the torsion, the harmonic oscillator partition function is found to be 1.77. As expected the correct treatment of internal rotation yields a larger value for the partition function, but the agreement between the two is quite close.

Since the barrier for CH_3 rotation here is expected to be smaller[20] than for the ethane case, it seems likely that the true partition function for this degree of freedom will be somewhat greater than the harmonic oscillator value used in the RRKM calculations. A larger partition function for the transition state would of course *increase* the activated complex theory rate constant. This in turn would result in poorer agreement with experiment, which is 65% of the standard (all vibrations treated as harmonic oscillators) activated complex theory result. Thus it appears unlikely that the harmonic oscillator treatment of the methyl rotation at the transition state is a source of the remaining disagreement between transition-state theory and experiment.

Concluding Remarks

The theoretical vibrational frequencies reported here for the $CH_3NC \rightarrow CH_3CN$ transition state are probably the most reliable obtained to date for a molecule of this size. This consistent reliability (~10%) makes ab initio calculations of activated complex and RRKM rate constants meaningful. At 500 K the experimental preexponential factor of Schneider and Rabinovitch[4] is 65% of that predicted from transition-state theory. Considering the limitations inherent in simple dynamical theories of the activated complex (transition state) or RRKM type, the agreement is encouraging. However, attempts to "invert" experimental rate constants (via the RRKM hypothesis) to infer transition state structural and vibrational parameters should probably be discouraged.

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Internal Rotations in Aliphatic Molecules: *n*-Butane and 2,2,3,3-Tetrafluorobutane

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Abstract: Rotational energy profiles for internal rotations about the central C–C bond of *n*-butane and 2,2,3,3-tetrafluorobutane (TFB) are calculated using ab initio and semiempirical quantum chemical methods. Extensive geometry optimizations are performed for each rotamer. The rigid rotor approximation is seen to provide an adequate representation in the trans-gauche transition region of *n*-butane but CCC bond angle optimizations are necessary in the vicinity of the syn conformer. Optimizations of several geometrical parameters are required for accurate results with the fluoro-substituted molecule. The approximate ab initio PRDDO method is in good agreement with minimal and extended basis set ab initio results for *n*-butane but furnishes poor energy differences and barriers for TFB. On the other hand, PRDDO does provide a cost-effective means of obtaining optimized geometries on which to perform ab initio calculations.

Internal rotations of molecules about covalent bonds play an important role in many branches of chemistry and biology. Much of the conformational freedom of proteins and nucleic acids arises from rotations about bonds involving C, N, O, and P atoms.[1,2] There is much evidence that the structural disorder and phase transitions observed in lipid bilayers[3] are a consequence of trans ↔ gauche rotational transitions about C–C bonds in saturated hydrocarbon domains.[3-5] Accurate po-

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