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Experimental and *ab Initio* Theoretical Study of the Kinetics of Rearrangement of Ketene Imine to Acetonitrile

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When heated by reflected shock waves to temperatures between 1400 and 1700 K at pressures of approximately 12−15 atm, mixtures of acetonitrile in argon (0.4−7 mol %) exhibit strong banded absorption in the ultraviolet region between 320 and 250 nm. The carrier of the absorption spectrum is ketene imine, $H_2C{=}C{=}NH$. Time-resolved spectra of ketene imine have been recorded with exposure times between 100 and 200 μs using a charge-coupled device (CCD) with an imaging spectrograph. Through the use of the technique of pixel binning, temporal profiles of formation and equilibration of ketene imine have been obtained with a time resolution of 24 μs. The rearrangement of ketene imine ↔ acetonitrile has been studied using *ab initio* quantum chemical techniques. The calculations predict the rate-determining step in the rearrangement process to be the 1,2-hydrogen transfer of the imine hydrogen to the adjacent carbon atom to produce vinyl nitrene. With the aid of the *ab initio* results, the experimental rate data for the reaction ketene imine → acetonitrile have been extrapolated to the high-pressure limit, yielding the rate constant expression $k_\infty = 10^{13.4(\pm0.5)} \exp(-294(\pm14)\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$.

Introduction

Isomers of formula C_2H_3N are considered to play an important role in interstellar space.[1,2] One such species is the transient molecule, ketene imine, $H_2C{=}C{=}NH$, a tautomer of acetonitrile and an important intermediate in reactions producing CH_3CN.

Ketene imine was first characterized in 1963 by Jacox and Milligan,[3] and subsequently, infrared and ultraviolet spectra of this molecule were obtained in an argon-isolated matrix through the interaction of acetonitrile with argon atoms in a microwave discharge.[4] Since that time, microwave spectra of gas phase ketene imine have been obtained[5,6] and a high-resolution infrared spectrum of the ν_4 band of the gas phase molecule has also been reported.[7] As yet, however, there does not appear to be any unambiguous observation of an electronic spectrum of gas phase ketene imine.

There have been several theoretical studies of ketene imine.[2,8−10] At the highest levels of theory calculations show the C=C=N skeleton to be slightly bent. From calculations made at the MP4/6-311+G level, Smith and Radom[10] predicted that the heat of formation of ketene imine at 298 K is 175 kJ mol^{-1}, a value that is only ~100 kJ mol^{-1} higher than the experimental heat of formation of acetonitrile, the most stable of the C_2H_3N isomers.

There have been two previous theoretical studies of the C_2H_3N potential energy hypersurface.[11,12] Both of these were principally concerned with the rearrangements of vinyl nitrene, produced by gas phase thermolysis of vinyl azide or 1*H*-1,2,3-triazole. These studies located several stationary points involving vinyl nitrene, 2*H*-azirine, methyl isocyanide, and acetonitrile and pathways connecting these points. The MNDO study[11] did not consider the pathway from ketene imine to acetonitrile. Whereas in the *ab initio* work of Lohr *et al.*[12] ketene imine was considered, Lohr *et al.* were unsuccessful in locating a transition state leading from ketene imine to acetonitrile by means of a 1,3-hydrogen shift.

Ketene imine has been detected in experimental studies, although it has been observed to rapidly rearrange into acetonitrile.[2,5,7] Ketene imine may be considered to be formally similar to the isoelectronic allene, $H_2C{=}C{=}CH_2$, with acetonitrile being the analogue of propyne, CH_3CCH. The rearrangements of these isoelectronic hydrocarbons have been studied extensively both experimentally[13,14] and theoretically.[13−16] For allene ↔ propyne the rate-determining step in the rearrangement is a 1,2-hydrogen shift. Therefore, it is plausible that an analogous mechanism exists for the ketene imine ↔ acetonitrile rearrangement. This idea is explored in the *ab initio* studies reported in this paper.

In addition, the electronic absorption spectrum of ketene imine, recorded behind reflected shock waves in acetonitrile dilute in argon and at temperatures between 1450 and 1650 K, is reported. The temporal variations in the spectrum are utilized in a study of the kinetics of the ketene imine ↔ acetonitrile reaction and the results compared with those obtained in the *ab initio* quantum chemical calculations.

Experimental Section

Spectroscopic and kinetic studies were made behind reflected shock waves in a shock tube of 76 mm internal diameter equipped with sapphire windows.[17] Time-resolved ultraviolet spectra were recorded using a Tektronix 512 × 512 pixel thermoelectrically cooled charge-coupled device (CCD) operated by a Princeton Instruments ST-138 controller and mounted at the exit plane of a Spex 270M imaging spectrograph. Spectra were measured using either a 600 or 300 grooves/mm grating enabling a spectral region of either 90 or 180 nm to be recorded at a spectral resolution of either 1 or 2 nm. Continuous radiation from a 150 W Cermax high-pressure collimated xenon lamp passed through the sapphire windows of the shock tube and was focused onto a 50 μm diameter fiber optic cable which conducted the radiation to the entrance slit of the spectrograph. The dispersed light existing from the spectrograph is focused onto the top 10 rows of pixels of the CCD chip. At the end of

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the exposure time, usually 100 μs, the charge accumulated in the top 10 rows is shifted into the storage area. The shifting time is 2.4 μs per row of pixels. After shifting is complete the second exposure begins, followed by a further shifting cycle. In the approximately 800 μs residence time behind the reflected shock front, about seven time-resolved spectra can be recorded.

When the charge stored by each of the 512 individual pixels in the wavelength direction is being read out, the exposure time necessary to obtain a signal to noise ratio of 10 or more cannot be reduced significantly below 100 μs. Since the major contribution to the noise of the output of the CCD chip, when using short exposures, is the readout noise, the signal to noise ratio can be greatly improved by "pixel binning" in the wavelength direction. Once the spectral region over which the ketene imine absorbed was established, 200 pixels across the wavelengths where only ketene imine absorbed were binned together. Readout noise was thereby so greatly reduced that the limit of time resolution became the time taken to shift the exposed region into the storage region, *i.e.*, 24 μs. Thus, to obtain profiles of the temporal variation in ketene imine concentration, pixel binning was employed.

Although the present work is principally concerned with the observation of the electronic absorption spectrum of ketene imine in shocked acetonitrile vapor and the kinetics of rearrangement to acetonitrile, several other precursors of ketene imine have also been studied in preliminary experiments in order to establish the validity of the ketene imine spectra. In addition to acetonitrile, butanenitrile, ethyl cyanide, allyl cyanide, crotononitrile, and 2-pentenenitrile were studied. In each case, the substance was prepared dilute in argon at concentrations between 0.4 and 7 mol %. Reactants were degassed by several freeze–pump–thaw cycles prior to use. Although the mixtures were made up manometrically, high-resolution gas chromatography was used to analyze the reactant mixtures and to test for impurities, which were always found to be below 0.5% of the concentration of the reactant. The precursor mixtures were then heated behind reflected shock fronts to temperatures between 1400 and 1700 K and pressures between 12 and 15 atm, allowing the recording of time-resolved spectra, as described above.

Computational Section

Quantum Chemical Calculations. Quantum chemical calculations were carried out using Hartree–Fock SCF, multiconfiguration SCF (MCSCF), and coupled cluster (with single and double excitations and perturbative correction for triples, *viz.*, CCSD(T)) methods.[18] The basis sets employed are Dunning's[19] double-ζ (DZ) and double-ζ plus polarization functions (DZP) (ζ_{3d}(C,N) = 0.8, ζ_{2p}(H) = 1.0), *i.e.* [4s,2p;2s] and [4s,2p,1d;2s,1p] contractions of (9s,5p,1d;4s,1p) primitive Gaussian bases. A significantly larger basis set, namely, Dunning's cc-pVTZ basis,[20,21] was also used in a few calculations, so as to test the adequacy of the DZP set.

The geometries of ketene imine and of the various intermediates that occur in the proposed reaction scheme were first optimized at the SCF/DZ level of theory, assuming closed shell configuration for all the species. The ground state of vinyl nitrene was however found to have a biradical type structure; hence its geometry was optimized using a restricted open shell Hartree–Fock (ROHF) formalism. The geometries of all the transition states and of most intermediates were reoptimized at the MCSCF/DZP level, using the complete active space SCF (CASSCF) method,[22,23] treating two electrons as active and employing an active space of 10 orbitals. In the transition states, where MCSCF effects are expected to be of some importance, the bonding between the migrating H atom (or CH_3 radical) and the rest of the molecule can be qualitatively described in terms of a two-electron three-center bond. Treating those two electrons as active may therefore be expected to provide a balanced description of the bonding in the transition state structures. The choice of such a large active space was motivated by the need to resolve adequately and reproducibly any mixing of the electronic states that may contribute to the transition state. Use of a small active space, such as two or four orbitals, yielded energies that at times appeared to correspond to local minima; inasmuch as depending on the starting wave function, different, apparently converged, MCSCF energies were obtained. No such problems were experienced with the 10-orbital active space. As expected, only the transition state geometries were found to be sensitive to the level of theory used; in the case of ketene imine, acetonitrile, and the various intermediates the SCF/DZ treatment was found to be adequate. At the appropriate optimized geometries the harmonic force constants were computed, thus enabling the calculation of zero-point corrections to the energies and of the thermodynamic functions that are needed in the RRKM analysis.

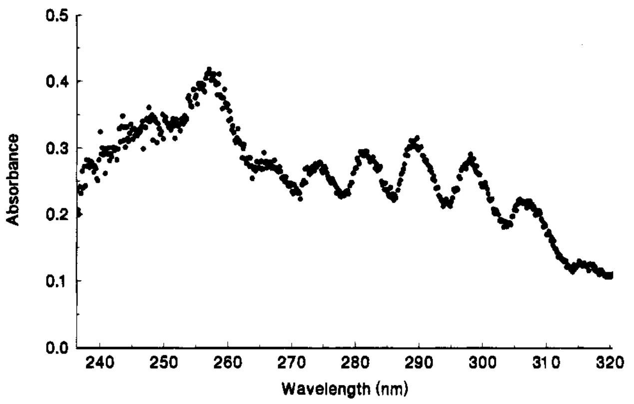

Figure 1. Ultraviolet absorption spectrum of shock-heated acetonitrile (6.7 mol % in argon) showing prominent ketene imine absorption. Exposure time, 225 μs, commenced 60 μs after arrival of the reflected shock. Temperature = 1676 K; pressure = 12 atm.

With the exception of the vinyl nitrene intermediate each of the species studied turned out to have wave functions that are dominated by a single closed shell configuration, thus enabling single reference based correlated calculations to be carried out, *viz.*, CCSD(T). In the latter computations the carbon and nitrogen 1s core orbitals were kept frozen to substitutions. The CCSD(T) energies, corrected for zero-point vibrations (using the SCF/DZ or MCSCF/DZP frequencies), are regarded as our best and most reliable.

The SCF geometry optimizations were carried out using the CADPAC5 programs,[24] while the MCSCF calculations were performed using the SIRIUS[25] and ABACUS[26] codes. The MOLECULE[27–29] and TITAN[30] programs were used for the CCSD(T) computations. The computations were performed on IBM6000/320 workstations.

Results and Discussion

Ultraviolet Spectra of Shock-Heated Nitriles. For each of the nitriles in this study, when shock heated to around 1500 K, the same common banded spectrum was observed at wavelengths between 250 and 320 nm. The strongest absorption was observed in shocked acetonitrile. Additional broad maxima not associated with the banded spectra were also observed with nitriles other than acetonitrile. The banded spectrum observed in 6.7 mol % acetonitrile in argon, shocked to 1676 K at a pressure of 12 atm is shown in Figure 1. This spectrum,

TABLE 1: Absorption Maxima of Ketene Imine in the Near-Ultraviolet (Wavelengths in nm)

	Jacox[4]		
this work	A[a]	B[a]	Callear & Lee[31]
317.0(±1)			
306.2(±1)	306.2	306.0	304.51
297.7(±1)	297.0	297.0	295.39
289.0(±1)		288.5	286.93
281.4(±1)		280.3	279.18
273.7(±1)	273.2	273.0	271.7
266.3(±1)			
256.9(±1)	258.0	257.8	258.0

[a] For the data of Jacox, column A refers to ketene imine formed by photolysis of acetonitrile, column B ketene imine formed by codeposition in an argon matrix by excited argon atoms.

common to all the shocked nitriles, is assigned to absorption by ketene imine through comparison with spectra that had been measured in an argon matrix by Jacox.[4] In Table 1 the positions of the bands obtained from measurements behind the reflected shock front are given along with the bands assigned to ketene imine by Jacox. Included in Table 1 are band maxima recorded at room temperature by Callear and Lee[31] in flashed crotononitrile and allyl cyanide. Although Callear and Lee tentatively assigned the spectrum to cyanoallyl radical, comparison of their maxima with those of Jacox suggests that the spectrum observed by Callear and Lee is that the ketene imine. It is useful to compare the absorption maxima obtained in this work with those of Callear and Lee since their measurements were carried out at room temperature on gaseous mixtures. As the spectra of Jacox were obtained in argon matrix isolation studies of ketene imine, the absorption maxima are at slightly higher wavelengths than in the gas phase.

As seen from the data in Table 1, there is good agreement between the band maxima obtained in this work and those of Jacox, despite the ~2 nm red shift in the latter when compared with the values of Callear and Lee. An explanation for the presence of such a shift in our results could be due to the broadness of the absorption maxima. All the maxima assigned to ketene imine in this work correspond to absorption bands which were typically 5 nm wide, making it difficult to locate the maxima accurately. The problem was exacerbated by the presence of noise in the recorded spectra. The errors quoted in Table 1 consequently indicate the range of possible positions of the absorption maxima, given the broadness of the peaks. The difference in temperatures between the experiments conducted in this work and those of Callear and Lee could also lead to a systematic difference in the positions of the absorption maxima. In our experiments the ketene imine absorption was observed at reflected shock temperatures typically greater than 1500 K. With a sufficient increase in the temperature the upper rotational states of ketene imine (in its ground electronic state) are expected to become appreciably populated, resulting in a red shift of the bands in the progression. Such a shift to higher wavelengths could then result in fortuitously close agreement with the spectra recorded by Jacox.

It is therefore concluded that the absorptions recorded in shock-heated acetonitrile and other nitriles are due to the formation of ketene imine. In addition to the UV-absorption maxima recorded by Jacox and by Callear and Lee two additional bands were observed in our work which are also assigned to ketene imine. These previously unobserved bands appear at 266 and 317 nm. The temporal behavior of these bands has been found to be identical to the rest of the ketene imine spectrum, suggesting that they do not correspond to absorption by another species. The two bands also appear at spacings from the adjacent bands that are consistent with the overall spacing in the main progression. The absorption at 266 nm is weak, and as it is a shoulder on the broad peak at 257 nm, it therefore may be difficult to observe under the experimental conditions of the earlier work. The weak band at 317 nm is most likely to be a hot band; it may well be impossible to observe at the lower temperatures of the previous studies.

As ketene imine and ketene are isoelectronic, we may expect a degree of similarity between their respective electronic spectra. This could aid with the actual assignment of the observed electronic transitions. Ketene displays a strong system of bands in the region of 213−193 nm with a vibrational spacing of ~1100 cm^{-1}, which is assigned to the CCO stretch.[32] This is followed by another system of bands[32] between 185 and 170 nm. In a fairly recent theoretical study Allen and Schaefer[33] assigned these two transitions as $\tilde{X}^1A_1 \rightarrow {}^1B_1$ and $\tilde{X}^1A_1 \rightarrow 2^1A_1$, respectively. Noting that both Jacox[4] and Callear and Lee[31] judged the 306−273 nm progression and the more intense peak at 258 nm of the ketene imine spectrum to be due to two distinct electronic transitions, the resemblance between the observed ketene imine peaks and those of ketene discussed above is quite compelling. On the basis of Allen and Schaefer's assignment for ketene we tentatively assign the observed transitions in ketene imine as being $\tilde{X}^1A' \rightarrow 2^1A'$ and $\tilde{X}^1A' \rightarrow 3^1A'$. We carried out some preliminary *ab initio* calculations on the low-lying excited states of ketene imine using the MCSCF method that suggest that the above assignment is reasonable. Much more work is needed however before a definitive assignment can be made on the basis of quantum chemical calculations. We plan to undertake such work in the near future.

The absorption bands of ketene imine are prominent in all the spectra that were obtained when mixtures of ethyl cyanide, butanenitrile, and allyl cyanide were shocked. In analogous studies of crotononitrile and 2-pentenenitrile the ketene imine absorption bands were also observed, but at a lower intensity. With the exception of butanenitrile the only energetically feasible pathway for the formation of ketene imine in these systems would be through a bimolecular free radical process. Such a process could also, of course, explain the formation of ketene imine from butanenitrile, although in this case the possibility of an intramolecular process should also be admitted, in light of the work of Ito *et al.*[7] In the latter study butanenitrile was pyrolyzed in a flow reactor to yield ketene imine in addition to other products of butanenitrile decomposition. Ito *et al.* used butanenitrile as a precursor to ketene imine because of the ease with which butanenitrile would undergo 1,5-H transfer to yield an intermediate which would decompose to form ketene imine and ethylene. The intensities of the ketene imine bands from shocked butanenitrile, as observed in our work, were however quite low, comparable with those observed in decomposing ethyl cyanide. This suggests that the intramolecular decomposition of butanenitrile to ketene imine and ethylene may only be a minor pathway in the shock tube decomposition of butanenitrile. This may not have been the case in the studies of Ito *et al.* since their experiments were carried out in a flow reactor where, in comparison with shock tubes, the residence time of the reaction is higher and consequently the temperature lower. The lower temperatures at which butanenitrile was pyrolyzed by Ito *et al.* would favor the formation of ketene imine and ethylene, since the reaction pathway involves a 1,5-H transfer. Such a reaction involves a transition state of low entropy relative to the reactants, but a relatively low activation energy. In the shock tube, the higher temperatures would favor bond fission processes, since, despite the high activation energy, the higher

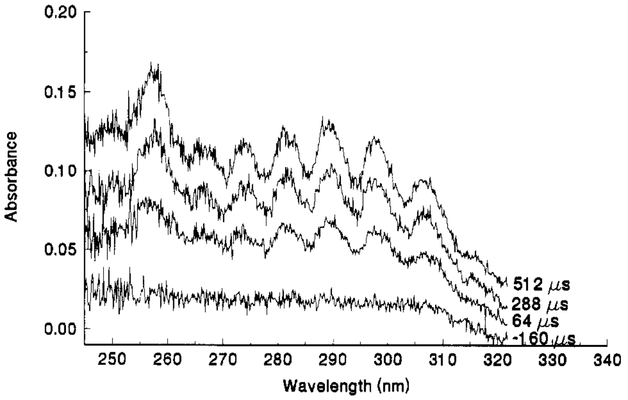

Figure 2. Successive UV spectra of a shocked mixture of acetonitrile (1.75 mol %) in argon showing growth with time in intensity of ketene imine absorption bands. Times indicate commencement of exposure relative to the arrival of the reflected shock front. Exposure time for each spectrum = 224 μs. Temperature = 1580 K.

A-factors would result in these reactions being favored over the low A-factor, low activation energy intramolecular processes.

Kinetic Studies. When mixtures of acetonitrile in argon are shocked to temperatures between approximately 1450 and 1550 K, the ketene imine absorption bands start to appear soon after the arrival of the reflected shock. When the absorption spectra are recorded at successive intervals of time after the reflected shock, the intensity of the ketene imine bands increases progressively, as shown in Figure 2. However, when the shocked gases are subjected to GC analysis, no detectable decomposition of the acetonitrile can be observed. At temperatures approaching 1600 K, the increase in band intensity with time levels out fairly rapidly to an equilibrium value. Yet it is only above 1600 K that significant decomposition of the acetonitrile becomes evident from the product chromatograms. At temperatures of 1670 K and above, the ketene imine bands, which are prominent immediately after the passage of the reflected shock, start to decrease rapidly in intensity over the residence time. At these temperatures, decomposition of acetonitrile is very rapid[34] so that the decrease in ketene imine band intensity must be associated with the disappearance of acetonitrile.

These observations are in accord with the occurrence of the tautomerization reaction, acetonitrile ↔ ketene imine, and this reaction equilibrates at temperatures below which any appreciable thermal decomposition of acetonitrile takes place.

Because of the limited time resolution, the temporal changes in intensity of the complete ketene imine spectrum could not be used for the measurement of ketene imine growth kinetics. To gather data on the rate of growth of ketene imine, the technique of pixel binning discussed above was used. This technique allowed changes in absorbance to be monitored with a time constant of 24 μs over the wavelength range 278–310 nm, where only ketene imine absorbs.

Typical growth profiles obtained at three different temperatures are shown in Figure 3, which demonstrate that as the reflected shock temperature increases, the initial rate of growth of ketene imine also increases. The approach to an equilibrium concentration of ketene imine is more easily observed as the reaction temperature increases.

Included in Figure 3 are the data obtained in a run conducted in pure argon. The absorbance trace for that run shows no increase with time, with any temporal variation being comparable with the noise level for the successive points. This experiment clearly demonstrates that the growth profiles of ketene imine absorbance are not the result of any experimental artifact.

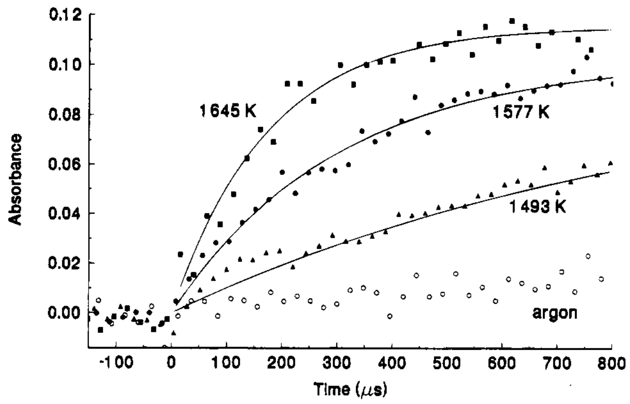

Figure 3. Profiles of ketene imine absorption versus time after arrival of the reflected shock front for a 1.8 mol % mixture of acetonitrile in argon. Also shown is a blank run in pure argon. Each point corresponds to an exposure time of 24 μs. Curves are the least squares fits to eq 4.

Calculation of the Rate Constant for Rearrangement of Ketene Imine to Acetonitrile. In order to extract rate constant information from the ketene imine growth profiles, two assumptions have been made. It has been assumed that the rate of the reverse reaction, the rearrangement of ketene imine to acetonitrile, is much faster than the rate of the forward reaction. It is also necessary to assume that the concentration of ketene imine at equilibrium is much smaller than the concentration of acetonitrile, and therefore the concentration of acetonitrile remains effectively constant even when equilibrium with ketene imine has been attained.

The arguments justifying these two assumptions depend on the large difference in the heat of formation between acetonitrile and ketene imine. As noted in the Introduction, this difference is expected to be ~100 kJ mol^{-1} when computed from the *ab initio* heat of formation of ketene imine calculated by Smith and Radom[10] and the experimental value for acetonitrile. Our calculations, to be discussed in detail later, suggest that the difference in the heats of formation is even higher, ~133 kJ mol^{-1}. The high endotherm of the rearrangement of acetonitrile to ketene imine suggests that only a small proportion of the acetonitrile would be converted to ketene imine at equilibrium, and therefore the reverse reaction of the rearrangement would be much faster than the forward one.

A more accurate estimate of the proportion of acetonitrile converted to ketene imine at equilibrium over the temperature range studied can be obtained by computing the equilibrium constant, K_{eq}, for the reaction. Heat capacities and entropies for ketene imine were calculated from our *ab initio* molecular constants, and together with literature values[35] of the thermochemical parameters of acetonitrile, K_{eq} was estimated to be 5×10^{-5} at 1700 K. In the absence of thermal decomposition such a value of K_{eq} at 1700 K would indicate that the concentration of acetonitrile would remain essentially constant during equilibration with ketene imine.

A comparison of the expected forward and reverse rates of reaction for tautomerization of acetonitrile could also be made by considering the relative rates observed for the analogous reversible rearrangement of propyne to allene.[13,14] The latter process differs from the acetonitrile ↔ ketene imine reaction in that allene and propyne have similar heats of formation. The activation energies for the forward and reverse reactions are therefore comparable, as shown by the work of Karni *et al.*[14] If the propyne to allene isomerization is analogous to the rearrangement of acetonitrile to ketene imine, the rate of the ketene imine to acetonitrile rearrangement should be much larger than that forward rate, *i.e.*, that for acetonitrile → ketene imine. This is because now the ketene imine → acetonitrile reaction is favored by the lower activation energy, as discussed above.

The kinetic parameters can be extracted from the ketene imine growth profiles using an equation derived from the following expression:

$$C_B = \frac{k_f A_0}{k_f + k_r}[1 - e^{-(k_f+k_r)t}] \qquad (1)$$

where C_B = concentration of ketene imine, k_f = forward rate constant (rate constant for ketene imine formation), k_r = reverse rate constant (rate constant for the formation of acetonitrile from ketene imine), and A_0 = initial concentration of acetonitrile.

Equation 1 applies to systems approaching equilibrium where the forward and reverse rates are comparable. If it is assumed that $k_f \ll k_r$ and that A_0 is very close to the concentration of acetonitrile at equilibrium (A_{eq}), eq 1 can be simplified to

$$C_B = \frac{k_f A_{eq}}{k_r}(1 - e^{-k_r t}) \qquad (2)$$

Since $k_f/k_r = K_{eq}$ for the acetonitrile ↔ ketene imine rearrangement, and if B_{eq} is the equilibrium concentration of ketene imine, then $K_{eq} = B_{eq}/A_{eq}$. Equation 2 thus becomes

$$C_B = B_{eq}(1 - e^{-k_r t}) \qquad (3)$$

Equation 3 is written in terms of concentration, whereas in the experiments the absorbance of ketene imine was measured. The concentrations C_B and B_{eq} can both be reexpressed in terms of the absorbance as

$$\text{abs}_B = \text{abs}_{eq}(1 - e^{-k_r t}) \qquad (4)$$

where abs_B = absorbance of ketene imine at time = t and abs_{eq} = equilibrium absorbance of ketene imine (*i.e.*, ketene imine absorbance at time → ∞).

It is apparent from eq 4 that the ketene imine growth profiles are functions of abs_{eq} and k_r. Although the changing ketene imine absorbances appeared to approach an equilibrium value at high temperatures, as can be seen from Figure 3, at lower temperatures the asymptotic approach to abs_{eq} could not be observed directly from the experimental abs_B profiles. The ketene imine absorbance profiles are therefore functions of two unknowns, abs_{eq} and k_r. These two variables were calculated from the ketene imine growth profiles using a nonlinear least squares fitting technique. The growth profiles were fitted to the exponential function given in eq 4 to yield abs_{eq} and k_r values to best fit the experimental absorbance profiles. The fitted curves are also shown in Figure 3, so a comparison with the experimental data points can be made.

A first-order plot of the rate constant of ketene imine to acetonitrile rearrangement is given in Figure 4. The temperature region for which the measured k_r was found to be reliable is 1480−1630 K. Below 1480 K the rate constant was too small to be measured with adequate precision because of excessive noise in the ketene imine growth profiles, while above 1630 K acetonitrile was found to undergo significant decomposition in the first 300 μs of the residence time. The assumption that the concentration of acetonitrile remains constant is therefore not appropriate under such conditions.

Linear regression analysis on the data presented in Figure 4 yields the following expression for the rate constant for the tautomerization of ketene imine to acetonitrile:

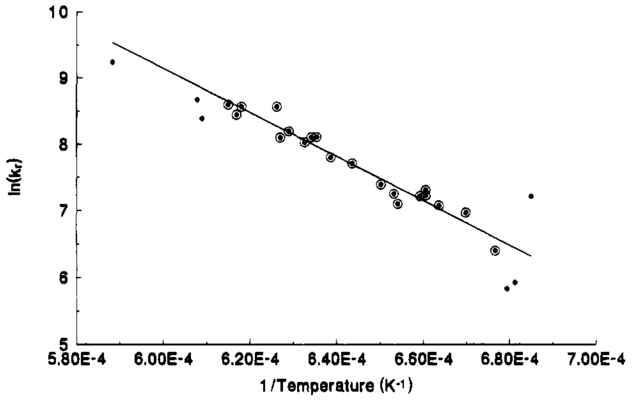

Figure 4. Arrhenius plot of the rate constant for rearrangement of ketene imine to acetonitrile, k_r: small circles, experimental data points; large circles, data used in regression analysis. The solid line is the regression fit.

$$k = 10^{12.6(\pm 0.5)} \exp(-277(\pm 14)\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$$

Comparison of the Arrhenius parameters given above with those of Karni *et al.*[14] shows that both the A-factor and the activation energy for ketene imine rearrangement are lower than the values for the analogous rearrangement of allene, although this comparison is not strictly valid, since the values of Karni *et al.* are the extrapolated high-pressure-limit Arrhenius parameters. By analogy with the allene/propyne system, at pressures of 11.5−14 atm the rate of rearrangement of ketene imine to acetonitrile is likely to be pressure dependent. An extrapolation to the high-pressure limit must therefore be made before any meaningful comparison of the rate parameters for the two systems can be made. We will return to this point after consideration of the quantum chemical results.

From the temperature dependence of abs_{eq} it should be possible to derive a value of the enthalpy of the reaction acetonitrile → ketene imine. However, the values of abs_{eq} obtained from the least squares fits to the experimental absorption profiles show significant scatter. There are several possible significant sources of error in the abs_{eq} values measured in this series of experiments.

The equilibrium concentration of ketene imine varies with the initial concentration of acetonitrile. However, in the experiments the initial concentration of acetonitrile only varied between 1.6 and 1.8 mol %, as measured by GC, and therefore the run-to-run variation in the initial concentration of acetonitrile is not the source of the scatter in the abs_{eq} data. The principal experimental error is in the measurement of the absolute values of the ketene imine absorbances. If the absolute values of the absorbance vary from run to run, the error contributes significantly and can be magnified in the evaluation of abs_{eq}. In most of the experiments conducted in this series, the measured absorbances of ketene imine were typically less than 0.2. The error in the measurements was such that it could result in an error of ±0.025 in the fitted abs_{eq} values and hence considerable scatter, particularly in view of the weak temperature dependence of the abs_{eq} data. Errors in the absolute absorbances have little effect on the fitted k_r values, since changes in the absolute absorbance would be analogous to changes in A_0, of which k_r is independent. Hence the k_r values show little scatter.

A test of the validity of the abs_{eq} values is to use the abs_{eq} data to obtain an estimate for the ΔH_{reac} (for the reaction acetonitrile ↔ ketene imine). By using the assumption that $A_0 = A_{eq}$, abs_{eq} can be expressed in terms of K_{eq} as

$$\text{abs}_{eq} = \epsilon d A_0 K_{eq} \qquad (5)$$

In eq 5 the average extinction coefficient of ketene imine over

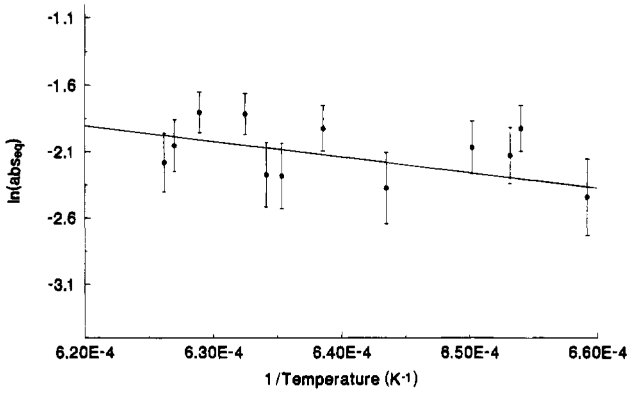

Figure 5. Plot of ln(abs$_{eq}$) versus inverse temperature. Error bars denote the estimated contribution of the error in absorbance measurement to abs$_{eq}$. The line represents the linear least squares fit to the data.

the wavelengths of the measurements (ϵ), the absorption pathlength (d), and the initial concentration of acetonitrile (A_0) are all constant from run to run. A plot of ln(abs$_{eq}$) versus $1/T$ should therefore be linear with a gradient of $-\Delta H_{reac}/R$. Such a plot over the temperature range 1510–1600 K is given in Figure 5, showing also the error bars that were calculated using the estimated error in the abs$_{eq}$ values of 0.025. It is apparent that the magnitude of the error in the abs$_{eq}$ measurements is comparable with the total variation of abs$_{eq}$ over the temperature range studied. This explains why the raw abs$_{eq}$ data appear to vary with temperature in a seemingly erratic manner. Nevertheless, if a linear regression analysis is performed on the data points of Figure 5, a value of $\Delta H_{reac} = 99(\pm 21)$ kJ mol^{-1} is obtained. This is consistent with the ΔH_{reac} value of 133($\pm$20) kJ mol^{-1} obtained from the *ab initio* calculations described below. Because of the large errors in our data, it would be inappropriate to suggest that our experimental value of ΔH_{reac} is reliable, but it does indicate that the abs$_{eq}$ values are consistent with the expected thermochemistry of the acetonitrile to ketene imine rearrangement.

Quantum Chemical Calculations. If we make the initial assumption that the ketene imine ↔ acetonitrile rearrangement is analogous to the allene ↔ propyne reaction, then we would expect the rate-determining step to be the 1,2-H transfer of the imine hydrogen to form vinyl nitrene. The proposed reaction pathway (I) then consists of the following series of reactions: ketene imine → vinyl nitrene (I1) → 2*H*-azirine (I2) → methyl isocyanide → acetonitrile. Alternatively, vinyl nitrene could rearrange directly to acetonitrile via a 2,3-H transfer (pathway II).

The optimized geometries of ketene imine, acetonitrile, and the various transition states and intermediates that are involved in the proposed reaction schemes are shown in Figure 6. The corresponding calculated total electronic energies and zero-point vibrational energies (ZPVE) are given in Table 2, while in Table 3 the energies relative to ketene imine are summarized.

The SCF/DZ and MCSCF/DZP geometries of ketene imine, as expected, were found to be in good agreement. For example, the differences in predicted bond lengths are less than 0.005 Å; thus, the energies quoted in Table 2 show little variation with geometry. Similar consistency is expected, or actually has been observed, for the other intermediates and the final product, *viz*., acetonitrile as well, so not all the geometries were optimized at the MCSCF/DZP level. The situation is potentially very different in the case of the transition states, as may be noted from the geometries that were obtained for TS1 and shown in Figure 6. Therefore, all the transition state geometries were optimized at the MCSCF/DZP level of theory.

The energies of the closed shell species were also calculated using the CCSD(T) method. On the basis of the MCSCF results it was expected that the wave functions would be dominated by the SCF reference state, and this has been borne out by the calculations. A better criterion for the applicability of the single-reference treatment, however, is the T_1 diagnostic of Lee and Taylor.[36] For the transition states, where the validity of single-reference wave functions is most in doubt, the values of T_1 obtained in the CCSD(T) calculations range from 0.021 to 0.025. While such values are indicative of some near-degeneracy, previous studies using the CCSD(T) method suggest that the method is sufficiently robust to resolve such near-degeneracies adequately.[37,38] By comparison, for the other species, such as the intermediates, the observed values of T_1 range from 0.011 to 0.015. We found, however, that the CCSD(T) energies differed substantially from what was obtained at the MP2 level. For example, in the case of the TS1–ketene imine energy difference, the MP2 value is ~38 kJ mol^{-1} larger than what is obtained in the CCSD(T) calculation. Therefore, no MP2 results are quoted.

The results obtained strongly suggest that the rate-determining step in the reaction is the formation of the intermediate I1, *viz*., vinyl nitrene, via the transition state TS1. The most stable electronic configuration of I1 was found to correspond to a biradical structure, *i.e*., open shell configuration; thus, TS1 represents a system whose electronic structure may be expected to be "between" the effectively closed shell configuration of ketene imine and the open shell biradical configuration of I1, with the possibility of the two configurations making comparable contributions to the wave function. This would make the geometry of TS1 potentially very sensitive to the nature and flexibility of the wave function, *viz*., the level of calculation. The SCF/DZ and MCSCF/DZP geometries are indeed quite different, as noted already, and this is further manifested in the large difference in the predicted critical energies: 261.2 and 315.4 kJ mol^{-1}, when calculated at the CCSD(T)/DZP level of theory at the SCF/DZ and MCSCF/DZP geometries, respectively. (Contrary to expectations, however, the MCSCF wave functions of TS1 were found to be strongly dominated by a single closed shell configuration, suggesting that the CCSD(T) method may be used.) Exploration of the potential energy surface in the vicinity of these two different geometries suggests that it is relatively flat at the MCSCF level of theory, varying by only ~10 kJ mol^{-1} between the two extremes. The large variation in the CCSD(T) energy is mostly due to the sensitivity of the correlation energy to geometry as well as the larger variation in the SCF energy itself, as shown by the data in Tables 2 and 3. Thus, a small bias in the MCSCF calculations may have a relatively large effect on the critical energy of the reaction, which we estimate as ~20 kJ mol^{-1}.

The sensitivity of the critical energy to basis set variations was also tested in the case of TS1 by recalculating it at the CCSD(T) level using a larger multiply polarized basis, including 4f functions on the heavy atoms, derived from Dunning's cc-pVTZ set.[20,21] As the full set proved too large for our current codes, it was truncated somewhat by removing the 3d functions from the two methylene hydrogens. The resulting critical energy is 329.1 kJ mol^{-1}, *i.e*., 13.7 kJ mol^{-1} higher than what had been calculated using the DZP basis. Thus the errors due to basis set incompleteness appear to be reasonably small, *viz*., ~4% of the critical energy.

The MCSCF calculations reported in this work, as noted above, are of the CASSCF type, and in the study of the rearrangement processes the active space consists of 10 orbitals, with two electrons treated as active. Test calculations with

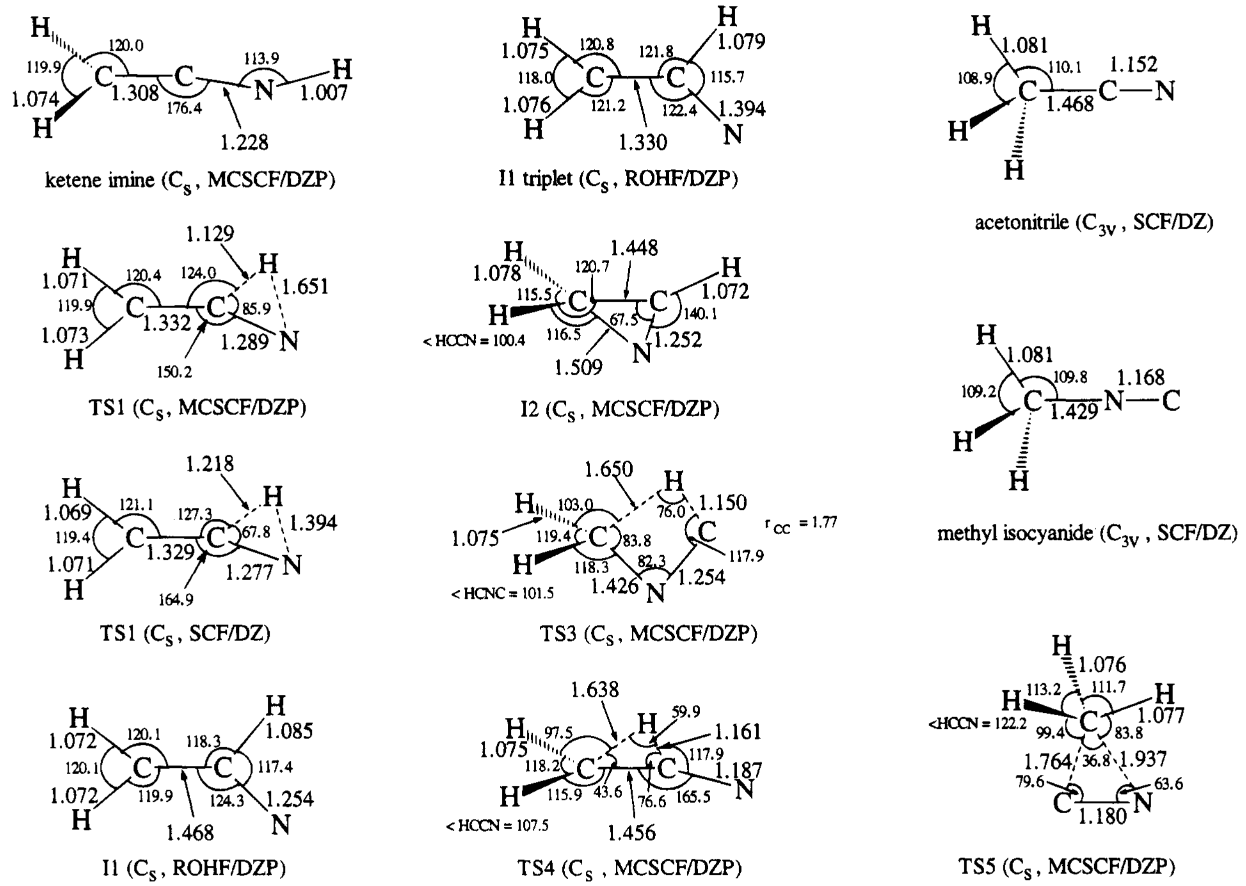

Figure 6. Optimized geometries (angstroms and degrees) for the various species in the proposed reaction pathways, indicating symmetry and level of calculation.

TABLE 2: Total (Singlet State) Energies (E_h) Calculated at the MCSCF/DZP Geometries (Figure 6), Unless Indicated Otherwise, and Zero-Point Vibrational Energies (ZPVE in kJ mol^{-1})

species	MCSCF/DZP^a	SCF/DZP^b	CCSD(T)/DZP^b	ZPVE
ketene imine	−131.933 15	−131.898 71	−132.352 36	121.9
	−131.931 61^c	−131.897 62^c	−132.351 15^c	123.9^c
TS1	−131.816 88	−131.784 56	−132.228 32	111.9
	−131.820 59^c	−131.791 41^c	−132.245 26^c	107.4^c
TS1 (triplet)	−131.828 01^d			
I1	−131.857 91^e	−131.854 69^e		115.5^e
I1 (triplet)	−131.877 03^e	−131.868 99^e		121.8^e
	−131.867 67^d			
TS2	−131.852 71^f			119.8^c
I2	−131.902 95	−131.863 36	−132.324 32	125.5
TS3	−131.818 51	−131.777 52	−132.256 64	112.5
TS4	−131.823 57	−131.773 35	−132.261 09	106.3
methyl isocyanide	−131.950 16^c	−131.919 93^c	−132.367 20^c	128.3^c
TS5	−131.876 92	−131.845 94	−132.300 24	118.9
acetonitrile	−131.984 54^c	−131.950 89^c	−132.403 50^c	128.5^c

[a] Basis with Cartesian 3d functions (six components). [b] Basis with spherical harmonic 3d functions (five components). [c] Calculated at SCF/DZ geometry and using SCF/DZ force field for ZPVE. [d] Calculated at geometry of corresponding singlet state. [e] Calculated at ROHF/DZP geometry and using ROHF/DZP force field for ZPVE. [f] Calculated at an approximate geometry (see text).

TABLE 3: Relative (Singlet State) Energies Including Zero-Point Vibrational Contributions (kJ mol^{-1})[a]

species	MCSCF/DZP	SCF/DZP	CCSD(T)/DZP
ketene imine	0.0	0.0	0.0
TS1	295.0	289.4	315.4
TS1	274.7^b	262.1^b	261.2^b
I1	191.0		
TS2	208.9		
I2	82.8	96.3	77.1
TS3	291.3	308.5	241.7
TS4	271.8	313.2	223.8
methyl isocyanide	−44.3^b	−54.1^b	−37.7^b
TS5	144.5	135.4	133.7
acetonitrile	−134.2^b	−135.1^b	−132.7^b

[a] Calculated from appropriate data in Table 2 at MCSCF/DZP geometries, unless indicated otherwise. [b] Calculated from energies at SCF/DZ geometries and using SCF/DZ force fields for ZPVE.

different parameters, *e.g.*, six active electrons and six active orbitals, which should describe correctly all the bond breaking and making processes that occur in the rearrangement of ketene imine to vinyl nitrene, yielded very similar geometries of TS1. Therefore, we feel confident that the geometries and energies obtained in this work are reasonably accurate and the estimated error in the critical energy, *viz.*, ±20 kJ mol^{-1}, is realistic.

The geometries of the lowest singlet and triplet states of I1, *viz.*, vinylnitrene, were found to be planar; thus, the electronic states are $^3A''$ and $^1A''$, corresponding to the configuration $\ldots 9a'^2 1a''^2 10a'^1 2a''^1$. The equilibrium bond lengths and the electron densities of these two species indicate, however, that in the triplet state the open shell orbitals are effectively localized on the nitrogen atom, while in the singlet state the 2a″ molecular orbital is localized on the methylene carbon atom, with the 10a′ MO being localized on the nitrogen. Thus, both species may be described as biradicals, but with different types of bonding: in the triplet there is a CC double bond and a CN single bond, while in the singlet there is a CC single bond and a CN double bond. The $^1A'$ closed shell state ($\ldots 9a'^2 1a''^2 2a''^2$ configuration) was estimated, on the basis of SCF results, to lie ~80 kJ mol^{-1} higher than the open shell ground state.

As the results in Tables 2 and 3 show, vinyl nitrene readily undergoes ring closure, forming the very stable intermediate I2, *viz.*, 2*H*-azirine, with a very low critical energy of reaction,

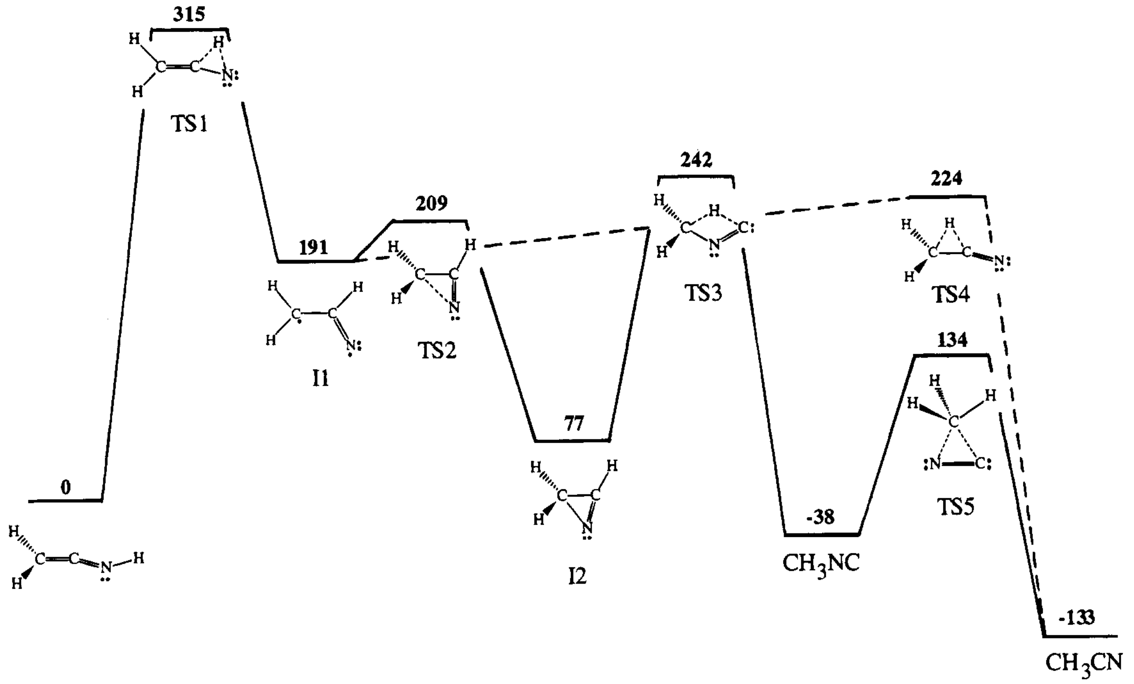

Figure 7. Reaction pathways and energetics for the rearrangement of ketene imine to acetonitrile. Pathway I is indicated by the solid line, whereas pathway II is indicated by the dashed line.

estimated to be ~18 kJ mol^{-1}. The determination of the corresponding transition state structure at the MCSCF level proved to be quite troublesome, probably due to the very shallow nature of the potential energy surface in the vicinity of the transition state TS2, so the above figure was actually obtained on the basis of pointwise MCSCF calculations on TS2 where first the CH_2 group of I1 was rotated by 90° followed by gradual decrease in the CCN angle. The energy was actually found to be maximum at (or very close to) the C_s geometry that was obtained by just rotating the CH_2 group. Given that this critical energy is of little importance in the overall reaction scheme, we did not think it worthwhile to persevere with the rigorous determination of the corresponding geometry at the MCSCF level. By comparison, the SCF/DZ optimized geometry is of C_1 symmetry, and the MCSCF energy at this latter geometry was found to be just 3.6 kJ mol^{-1} lower than at the "approximate" MCSCF geometry described above.

2*H*-Azirine (I2) can then form methyl isocyanide in a ring-opening reaction, via the transition state TS3. The critical energy of this reaction is also very sensitive to the level of theory used. As in the case of TS1, we consider the CCSD(T) calculation, carried out at the MCSCF geometry, as the most accurate for TS3; thus, its energy is expected to be well below or, at worst, comparable with that of TS1.

As is already well-known, the isomerization of methyl isocyanide to acetonitrile is a facile, low activation energy process, and our results are entirely consistent with the earlier findings. The critical energy of the reaction predicted by our CCSD(T) calculations is 171.4 kJ mol^{-1}, which is in good agreement with Collister and Pritchard's[39] experimental value of E_∞, *viz.*, 159.7 kJ mol^{-1}, as well as the earlier values obtained by Schneider and Rabinovitch[40] for E_0, *viz.*, 158.2 and 159.3 kJ mol^{-1}, depending on the vibrational model used.

As our results indicate, however, there is an alternative pathway (II) for the ketene imine → acetonitrile rearrangement, *i.e.*, 2,3-hydrogen migration in vinyl nitrene (I1), resulting directly in acetonitrile via the transition state TS4. The energetics of the latter process are comparable with those for pathway I discussed above.

The results of the calculations corresponding to the two reaction pathways, I and II, are also summarized in Figure 7, in an energy level type diagram, showing also what we believe to be the best Lewis structures of the various species. The bonding of the bridging hydrogens in the transition states (methyl in TS5) is best described as two-electron three-center bonds that are shown as dotted lines.

Two other possible pathways were also considered, namely, 1,3-hydrogen shift in ketene imine that would lead directly to the formation of acetonitrile and the ring-closing reaction leading to the formation of the cyclic intermediate $H_2C(NH)C$ (2*H*,*NH*-azirine). In the study of the isoelectronic reaction of allene → propyne Honjou *et al.*[15] as well as Kakumoto *et al.*[14] found that the critical energy of reaction of the 1,3-H migration is ~400 kJ mol^{-1}, that is, ~110 kJ mol^{-1} higher than required for the 1,2-H migration, which in allene, too, has been found to be the rate-determining step. We have been unable to find a transition state associated with 1,3-H migration in ketene imine. A saddle point was located at a geometry that closely resembles that of the transition state in the allene system, but as well as a very high energy (~470 kJ mol^{-1} above ketene imine), it had two imaginary frequencies, one corresponding to a mode that would tend to make the geometry planar and the other representing a mode that resembles the reaction coordinate in allene. However, when the molecule was allowed to become planar, it simply collapsed to TS1 or TS4, depending on the actual starting geometry. Therefore, we doubt that a transition state representing direct 1,3-H migration in ketene imine exists at all. A transition state was located for the reaction that would lead to the formation of the cyclic intermediate $H_2C(NH)C$, but the critical energy of such a process, estimated to be ~360 kJ mol^{-1} (on the basis of MCSCF and CI(SD) calculations), is significantly higher than what had been obtained for the 1,2-H shift, so the latter mechanism was discounted and not explored further.

Since Lohr *et al.*[12] have carried out quantum chemical calculations on most of the molecules studied in this work, a brief comparison of the respective results is in order. The agreement is generally good with regard to the relative stabilities, once allowances are made for the different levels of theory and basis sets, with one important difference. The stability of vinyl nitrene in its triplet state is greatly overestimated in the work of Lohr *et al.*; it is predicted to be ~3 kJ mol^{-1} more stable than ketene imine, whereas according to our MCSCF calculations, ketene imine is the more stable form, lying ~147 kJ mol^{-1} below vinyl nitrene. The discrepancy is due to the use of the unrestricted Hartree–Fock (UHF) method by Lohr *et al.* in the calculation of the triplet state energy. We repeated the calculations of Lohr *et al.* and reproduced their result, but we went one step further and calculated also the projected unrestricted MP2 (PUMP2) energy[41,42] of vinyl nitrene in its triplet state. When the resulting PUMP2 energy is compared with the MP2 energy of ketene imine, the latter is found to be more stable by 176 kJ mol^{-1}.

Determination of k_∞ for the Ketene Imine → Acetonitrile Rearrangement. Our *ab initio* calculations have shown that the critical energy for the rearrangement of ketene imine to acetonitrile is the reaction step involving the 1,2 transfer of the imine hydrogen to the immediately adjacent carbon atom. The species TS1 is therefore the transition state that needs to be used in a detailed RRKM treatment of the reaction and in solving the appropriate master equation.

Since the rearrangement of ketene imine is intramolecular, the change in angular momentum for the reaction would be small. Calculation of the high-pressure rate constant may be therefore performed without corrections for changes in angular momentum.

Extrapolation to the high-pressure limit was carried out using the program UNIMOL, which employs the weak collision treatment of falloff.[43] The *ab initio* optimized geometries (in the form of rotational constants) and harmonic vibrational frequencies of ketene imine and of the transition state TS1 were used as input data for the determination of the high-pressure-limit value of the A-factor and in the RRKM and master equation evaluation of the high-pressure rate constant. Although it is common practice to scale vibrational frequencies to account for the systematic errors due to the harmonic approximation and shortcomings of the *ab initio* calculations, the frequencies were not scaled in this case since both the reactant and transition states contain such errors and hence some cancellation of errors occurs. (However, we have carried out a high-pressure extrapolation using frequencies scaled[44] by 0.9 and find that the scaling makes virtually no difference to the computed Arrhenius parameters.)

Other input data required for the calculation of the high-pressure rate constant were obtained by analogy with similar species. UNIMOL requires the Lennard-Jones hard sphere collision diameter and well depth for the reactant/bath gas combination in the falloff calculations. These are not known for the ketene imine and argon system. However, the analogous Lennard-Jones hard sphere collision diameter and well depth are available for propyne, and considering the similarity of propyne to ketene imine, use of the values published for propyne[45] in the pressure extrapolation is not expected to introduce significant errors into the calculation.

In obtaining the high-pressure-limit rate constant for the ketene imine → acetonitrile rearrangement using UNIMOL, the critical energy of the rearrangement was adjusted so as to best fit the experimental values. Using the experimental Arrhenius expression, a falloff rate constant for rearrangement was calculated at 1300, 1400, 1500, and 1600 K. The critical energy was then varied to obtain optimal fit of the rate constants calculated using UNIMOL to the experimentally derived rate constants. The optimum value for the critical energy was found to be 290 kJ mol^{-1}. The experimental and predicted rate constants for this value of the critical energy are given in Table 4, along with the rotational constants and vibrational frequencies that had been used in the RRKM calculations.

TABLE 4: RRKM Extrapolation of Rate Data for the Ketene Imine → Acetonitrile Rearrangement[a]

temp/K	$\log(A_\infty/\mathrm{s}^{-1})$	$E_\infty/\mathrm{kJ\ mol}^{-1}$	k_∞/s^{-1}	k/k_∞	$k_{\mathrm{calc}}/\mathrm{s}^{-1}$ [b]	$k_{\mathrm{exp}}/\mathrm{s}^{-1}$ [b]
1300	13.35	293.3	32.7	0.92	29.9	33.6
1400	13.36	293.6	229	0.87	200	209
1500	13.36	294.0	1240	0.82	1010	1020
1600	13.37	294.2	5430	0.75	4090	4080

[a] Molecular constants: Ketene imine: $A = 202\,588$, $B = 9707.15$, $C = 9526.08$ MHz. $\omega_i = 3752, 3346, 2178, 1573, 1217, 1140, 870.3, 503.8, 3450, 1062, 948.0, 364.4$ cm^{-1}. Transition state TS1: $A = 116\,456$, $B = 10\,441.4$, $C = 9582.29$ MHz. $\omega_i = 3470, 3360, 2960, 1835, 1590, 1292, 1119, 747.7, 905.3, 793.7, 648.9$ cm^{-1}. [b] Rate constants k_{calc} and k_{exp} are specific rate constants for the experimental average pressure of 12.2 atm. An average collisional energy transfer of 700 cm^{-1} was used in the falloff calculations.

The calculated Arrhenius expression for the high-pressure rate constant over the temperature range 1300–1600 K was found to be

$$k_\infty = 10^{13.4(\pm 0.5)} \exp(-294(\pm 14)\ \mathrm{kJ\ mol}^{-1}/RT)\ \mathrm{s}^{-1}$$

with the errors in the above expression corresponding to the errors in the experimentally derived falloff rate parameters. The critical energy of 290 kJ mol^{-1} is in good agreement with the corresponding *ab initio* value of 315 kJ mol^{-1}. The theoretical value is slightly higher than the experimental figure, as also found in the case of the methyl isocyanide → acetonitrile isomerization.

Since the mechanism of ketene imine ↔ acetonitrile rearrangement appears to be analogous to that of allene ↔ propyne, the Arrhenius parameters of the two rearrangements are expected to be similar. Comparison of the high-pressure rate data[13,14] for allene ↔ propyne with those obtained for the ketene imine ↔ acetonitrile rearrangement indeed shows a high degree of similarity. In particular, the rate constant for the allene rearrangement, as found by Karni *et al.*,[14] is

$$k_\infty = 10^{14.03} \exp(-296\ \mathrm{kJ\ mol}^{-1}/RT)\ \mathrm{s}^{-1}$$

Clearly, the barriers to 1,2-H shifts are remarkably similar in the $=\!C\!=\!C(H)_2$ and $=\!C\!=\!N(H)$ systems.

Conclusions

At temperatures which preclude significant thermal decomposition acetonitrile can rearrange to ketene imine, which can be detected by its electronic absorption spectrum between about 320 and 250 nm. The unimolecular rearrangement kinetics of ketene imine → acetonitrile have been measured over the temperature range 1480–1630 K and the high-pressure rate constant found to be given by $k_\infty = 10^{13.4(\pm 0.5)} \exp(-294(\pm 14)\ \mathrm{kJ\ mol}^{-1}/RT)\ \mathrm{s}^{-1}$. Quantum chemical calculations indicate that the rate-determining step is the 1,2-hydrogen transfer of the imine hydrogen to form vinyl nitrene.

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