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Photodissociation of Methacrylonitrile at 193 nm: The CN Radical Product Channel

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Photodissociation dynamics of methacrylonitrile ($H_2C{=}C(CH_3)CN$) and 2-butenenitrile at 193 nm have been investigated by measuring laser induced fluorescence spectra of CN fragments. From the spectra, internal and translational energy distributions of CN have been obtained. For both molecules, the measured energy distributions are well represented by statistical prior calculations, assuming the CN and allyl radical products rather than the propenyl isomer. Ab initio calculations were performed for the relevant product species and transition states for isomerization and CN elimination. It has been concluded that methacrylonitrile dissociates in the ground electronic state via allyl cyanide formed by CN and H atom migration prior to dissociation. The quantum yield of the CN channel from methacrylonitrile was measured to be 0.012 ± 0.001.

Introduction

Studies of photodissociation dynamics of compounds containing C=C double bonds have been of considerable interest for many years because these molecules, upon UV irradiation, can produce molecular products via molecular elimination pathways and radical products via simple bond cleavages. Measurements of their relative yields between those channels and the dissociation dynamics were focused on in the studies of, for example, photodissociation of haloethylenes.[1–6] On the other hand, UV absorption spectra of cyanoethylene (acrylonitrile) were measured by Mullen and Orloff,[7] where the absorption around 190 nm is assigned to the $\pi \rightarrow \pi^*$ transition. Upon absorption at 193 nm, the CN radical elimination channel from acrylonitrile was investigated using transient frequency-modulation spectroscopy.[8] The measured quantum yield was 0.003, implying this channel is minor, and the translational energy distribution measured from Doppler profiles was well fitted to

the statistical prior calculation, from which it has been concluded that the dissociation takes place in the ground electronic state following internal conversion. Blank et al. thoroughly examined the photodissociation of acrylonitrile at 193 nm by photofragment translational spectroscopy using synchrotron radiation for photoionization of the fragments.[9] From the measured translational energy distributions of H, H_2, CN, and HCN fragments, they concluded that, again, the rapid internal conversion to the ground electronic state occurs followed by elimination of those four fragments. From the product branching ratio and the calculated RRKM dissociation rates, 2×10^{-4} (CN/HCN channel), the molecular elimination channels were identified to be the major channels. In addition, the measured translational energy distributions reflect statistical simple bond rupture for the radical channels while the molecular elimination channels have substantial recombination barriers.

Very recent studies on the photodissociation of 2-butenenitrile and 3-butenenitrile (allyl cyanide) at 193 nm producing CN

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demonstrated another example of the statistical unimolecular dissociation.[10,11] The dissociation takes place from the ground electronic state after the internal conversion from the initially prepared state, as in the case of acrylonitrile. The difference is whether the sibling fragment is a propenyl or a more stable allyl radical instead of the vinyl radical from acrylonitrile. In the case of 2-butenenitrile, frequency-modulated diode laser absorption spectroscopy was employed to measure the Doppler profiles in the spectra of the CN fragments. It was found that, rather than producing the propenyl, H atom migration to form allyl cyanide takes place prior to dissociation and that the translational energy distribution of CN appears to be in good agreement with the results of statistical calculations.

In this article, the photodissociation dynamics of methacrylonitrile ($H_2C=C(CH_3)CN$) at 193 nm and of 2-butenenitrile for comparison have been investigated by measuring rotationally resolved laser induced fluorescence spectra of the CN fragments. As in the cases of allyl cyanide, statistical unimolecular decomposition would be expected after absorption of a photon at 193 nm followed by internal conversion to the ground electronic state. An interesting point to be addressed is whether the dissociation products would be the allyl and CN radicals. The measured rotational population distributions and translational energy releases in the products are well represented by statistical calculations assuming an allyl radical product rather than the propenyl. The detailed dissociation dynamics of such a channel are discussed.

Experiments

The experiments were performed in a flow cell with conventional pump−probe geometry. The cell was evacuated at a pressure of about 10^{-3} Torr with a mechanical pump, and the gaseous sample was continuously flowed through the cell at a pressure of 20 mTorr. The liquid sample of 99% stated purity was purchased from Aldrich and used without further purification.

The unpolarized photolysis light at 193 nm obtained from an Excimer laser (Lambda Physik Lextra 50, typically 5 mJ/pulse, shaped as a 5 mm diameter circle) was introduced to the cell through an arm in which baffles were placed to minimize the scattered radiation into a detector. The probe light to measure the laser induced fluorescence (LIF) spectra of the CN fragments was the output of a dye laser (Lumonics H-500) pumped by the third harmonic of an Nd:YAG laser. The power of the probe laser light was kept as low as possible, typically 20 μJ/pulse, to avoid saturation in the spectra. The two laser beams were collinearly counterpropagated through the cell with a pump−probe delay time of about 100 ns. The 20 mTorr sample pressure and 100 ns delay between the lasers ensure nascent product quantum state distributions are probed. The LIF spectra of CN were measured employing the (0,0), (1,1), and (2,2) vibrational bands in the B ← X electronic transition between 388.5 and 382 nm. The induced fluorescence was measured with a photomultiplier tube (Hamamatsu, 1P28A) at a right angle to the laser beams through an appropriate cutoff filter. The detected signals were fed to boxcars and processed in a signal processor and PC. The powers of the photolysis and the probe lights were separately measured using photodiodes, and the measured fluorescence spectra were corrected for variation of the laser intensities.

Results and Discussion

A. Spectra and Internal Energies of the CN Fragments. The measured LIF spectra of CN from photodissociation of
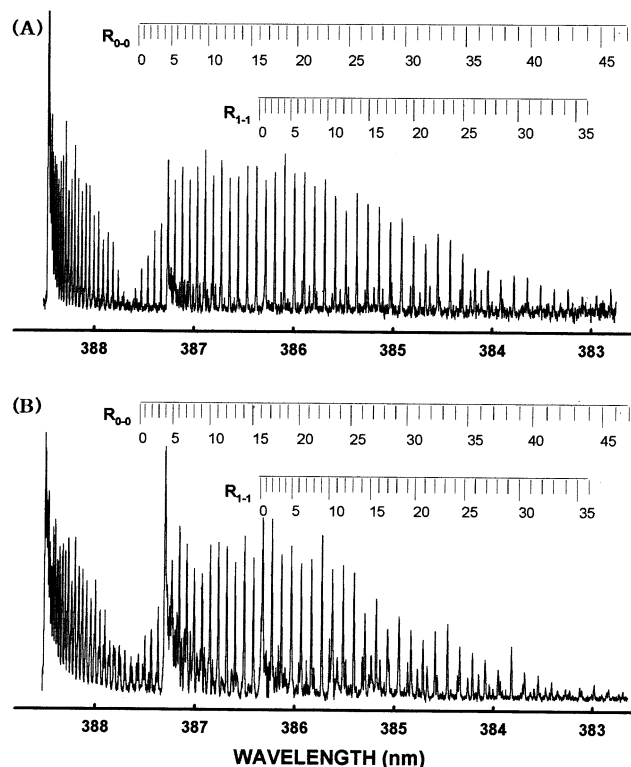

Figure 1. Laser induced fluorescence spectra of CN produced from photodissociation of (A) 2-butenenitrile and (B) methacrylonitrile at 193 nm employing the B ← X electronic transition.

methacrylonitrile and 2-butenenitrile at 193 nm are presented in Figure 1. The bandheads of the P-branch rotational transitions in the 0−0 and 1−1 vibrational bands are clearly observed, and the assignments are given above the spectra for the R-branch transitions.[12] Rotational population distributions were obtained from the relative intensities of the peaks corrected by appropriate line strength factors.[13] From the Boltzmann plots, the rotational temperatures were measured to be 1610 and 1290 K for $v'' = 0$ and 1, respectively, for methacrylonitrile while they were 1620 and 1300 K for 2-butenenitrile (Figure 2). The measured average rotational energies in CN are thus 13.4 ± 0.5 and 10.8 ± 0.5 kJ/mol for $v'' = 0$ and 1, respectively, from methacrylonitrile while they are 13.5 ± 0.6 and 10.9 ± 0.5 kJ/mol from 2-butenenitrile. The average rotational energies in CN from 2-butenenitrile and methacrylonitrile at 193 nm appear to be almost the same. In addition, vibrational population distributions were obtained from the integrated intensities of the peaks from the 0−0 and 1−1 rovibrational transitions by employing reported Franck−Condon factors[14] and are 0.77/0.23 for $v'' = 0/1$ for methacrylonitrile and 0.81/0.19 for 2-butenenitrile, respectively.

B. Absorption Spectra and Quantum Yields. The UV absorption spectra of 2-butenenitrile and methacrylonitrile vapor were measured and are presented in Figure 3. The spectra show in both molecules broad absorption with diffuse structures around 200 nm. Similar UV spectra of acrylonitrile were reported where the broad absorption near 200 nm is assigned as the $\pi \rightarrow \pi^*_{C=C}$ transition and the diffuse structures are responsible for the vibrational transitions in mainly the C=C stretch and C−C≡N bending modes.[7] If the same arguments could be applied for 2-butenenitrile and methacrylonitrile, the absorption at 193 nm would be responsible for the electronic transition to the allowed $\pi^*_{C=C}$ state from which the dissociation occurs.

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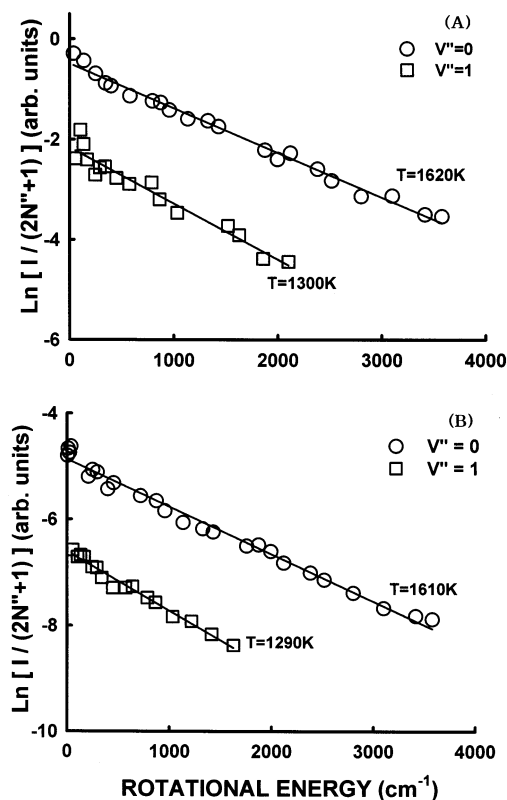*J. Phys. Chem. A, Vol. 107, No. 22, 2003* **4335**

Figure 2. Boltzmann plots of the rotational distributions obtained from the spectra in Figure 1 for (A) 2-butenenitrile and (B) methacrylonitrile.
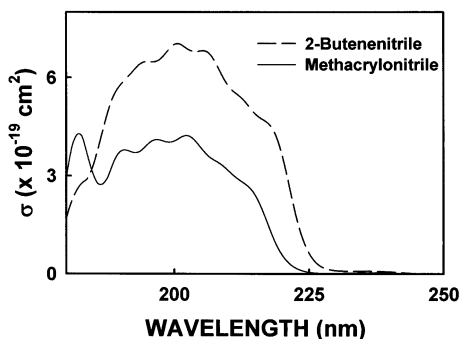

Figure 3. UV absorption spectra of 2-butenenitrile and methacrylonitrile vapor obtained by the SCINCO S-2180 spectrophotometer.

Figure 4. Doppler profiles of the $R_{00}(3)$ transitions of CN in the B ← X transition (A) after collisional relaxation, (B) from photodissociation of 2-butenenitrile, and (C) from photodissociation of methacrylonitrile. A dotted line is the CN Doppler profile at 300 K, dashed lines are the laser line profiles, and solid lines are the Doppler profiles obtained from the best fit by convolution of the laser line and CN Doppler.

Upon absorption at 193 nm, the parent molecules can dissociate into radicals and/or molecular elimination products such as HCN. The quantum yield of the minor CN radical channel from 2-butenenitrile at 193 nm was measured to be 0.01.[10] The quantum yield of the CN channel from methacrylonitrile can be measured by monitoring the CN radicals compared to those produced from relatively simple molecules such as BrCN or ClCN. However, the quantum yield for the CN radical channel from methacrylonitrile was, for convenience, relatively measured from the integrated LIF signal intensities of CN and the absorption cross section at 193 nm from 2-butenenitrile, since the quantum yield from 2-butenenitrile has been known. The measured quantum yield of the CN radical channel from methacrylonitrile is 0.012 ± 0.001.

C. Translational Energies of the CN Fragments. To measure translational energies of the fragments, the Doppler profiles of the individual rotational transitions in the spectra were measured. The laser line width was first measured from the rotational line profile after translational relaxation by collisions. In Figure 4, the measured line profile for the $R_{00}(3)$
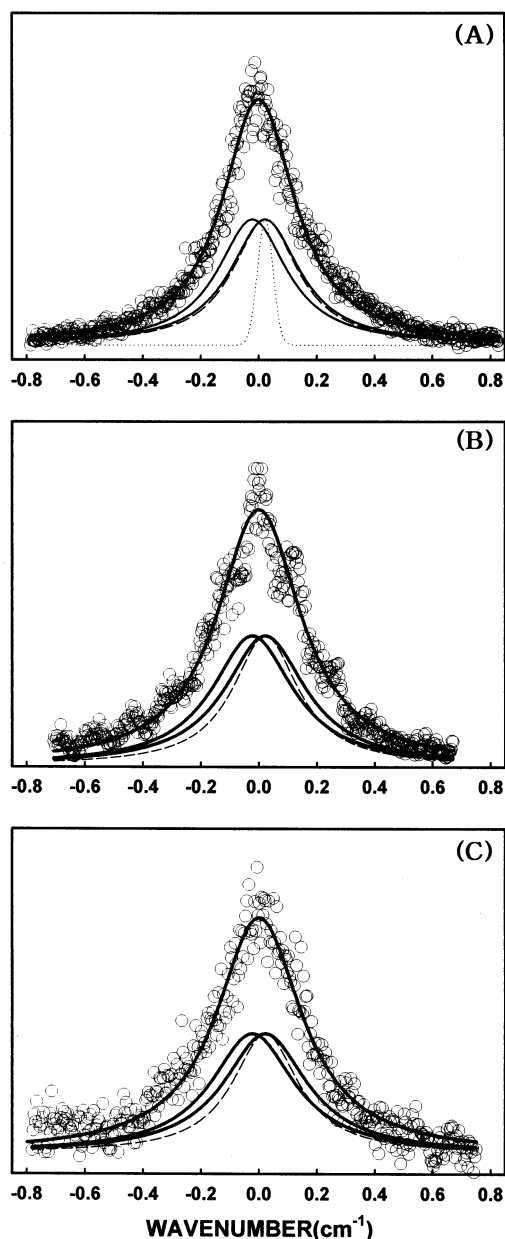
transition obtained at the 2 μs pump−probe delay and 5 Torr Ar as a collision partner is presented. At higher pressures of Ar, no changes in the measured profiles were observed. Under this condition, rotational relaxation to 300 K was observed, as demonstrated in Figure 5. The measured line profile was fitted by the Gaussian Doppler profile of CN at 300 K convoluted with the expected Lorentzian laser line profile. The measured fwhm of our laser line width is 0.27 cm^{-1}.

In Figure 4, the Doppler broadened spectra for $N = 3$ in the R-branch rotational transitions from 2-butenenitrile and methacrylonitrile are presented. It has been known that the angular momentum couplings in CN are governed by the so-called Hund case b.[15] In this case, the rotational energy levels in the X $^2\Sigma$ and B $^2\Sigma$ states are split into $J = N \pm \frac{1}{2}$ levels and the splitting grows as N increases. Thus, given the resolution of our laser, the rotational transitions from + and − levels are nearly
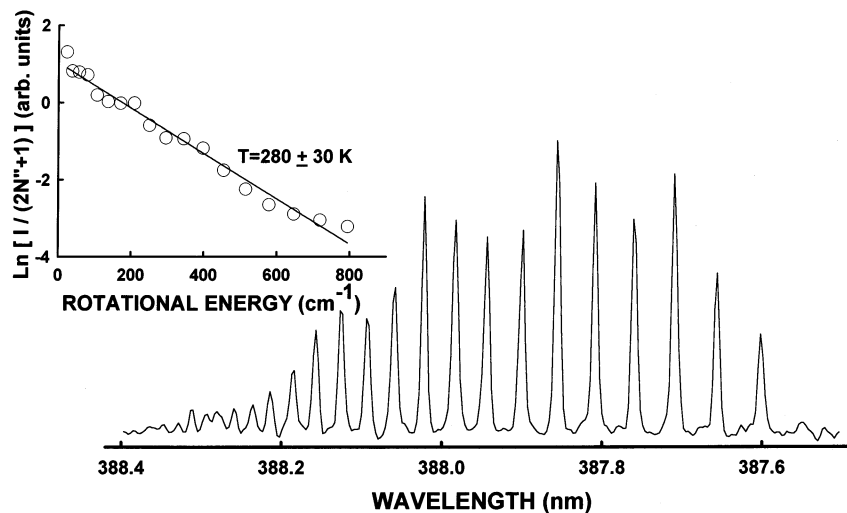
Figure 5. LIF spectra of CN for the P-branch rotational transitions after collisional relaxation. The inset is a Boltzmann plot obtained from the spectra.

TABLE 1. Energy Partitioning in the Products from Photodissociation of 2-butenenitrile and Methacrylonitrile at 193 nm (kJ/mol)

	2-butenenitrile			methacrylonitrile		
	measured	prior I[a]	prior II[b]	measured	prior I[a]	prior II[b]
$\langle E_r(CN)\rangle$	13.5 ± 0.6	10.0	14.1	13.4 ± 0.5	9.4	14.0
$\langle E_T \rangle$ for CN(v''=0,N) with N = 3	30.8 ± 2.5	18.6	28.1	34.4 ± 4.5	17.8	28.4
N = 4	32.8 ± 3.1	18.6	28.0	33.2 ± 3.2	17.8	28.4
N = 41	30.6 ± 4.0	13.1	23.7	33.2 ± 4.2	12.1	24.0
N = 43	30.6 ± 3.3	12.5	23.2	33.9 ± 4.5	11.5	23.6

[a] CN + propenyl radical channel. [b] CN + allyl radical channel.

overlapped at low N and almost resolved at high N. At N = 3, the separation of the two transitions is expected to be 0.05 cm⁻¹. The observed profile was fitted by convolution of the laser line profile with the expected Doppler profile of CN assuming a Gaussian velocity distribution. Then, the average translational energy was obtained from the second moment of the Gaussian profile obtained from the best fit. The center of mass translational energy releases are then 30.0 ± 2.5 and 34.0 ± 4.5 kJ/mol for 2-butenenitrile and methacrylonitrile, respectively. The measured average translational energy releases at CN (v'' = 0,N) for N = 4, 41, and 43 are listed in Table 1, and they are relatively invariant for the rotational levels of CN.

D. Dissociation Mechanism. The electronic transition at 193 nm leads the parent molecule to the excited singlet $\pi^*_{C=C}$ state, from which the dissociation takes place. However, since the excited singlet state resulting from the allowed $\pi \rightarrow \pi^*$ transition correlates to either one of the product radicals being in the first excited electronic state, the dissociation should take place from either the ground singlet state or the excited triplet states. Thus, it can be concluded that, as in acrylonitrile[8,9] and allyl cyanide,[11] the 193 nm electronic transition also leads to the excited singlet state followed by internal conversion and that statistical unimolecular dissociation takes place from the vibrationally hot ground state.

To study the detailed dissociation dynamics, the energy distribution in the products has been examined from model calculations. The dissociation energy was first calculated for the propenyl and CN radical channel from methacrylonitrile by ab initio calculations. The calculations were performed using the G2 theory proposed by Pople et al.[16] utilizing the Gaussian program package.[17] The calculated dissociation energy of 2-butenenitrile is 565 kJ/mol while it is 550 kJ/mol in the literature.[10,18] For methacrylonitrile, the calculated dissociation

energy is 551 kJ/mol and the accuracy of the calculation would be similar to that for 2-butenenitrile. Thus, at 193 nm, the available energies (photon energy, 620 kJ/mol, + internal energy of the parent molecule, 14 kJ/mol, − dissociation energy) that should be distributed in the products are 83 kJ/mol for methacrylonitrile and 84 kJ/mol for 2-butenenitrile, respectively. Then, a statistical prior model was employed to obtain the rotational energy distribution of CN.[19,20] In this model, it is assumed that the available energy should be distributed among all degrees of freedom of the products with equal probability. Thus, the population of the individual rotational state of CN would be proportional to the number of accessible quantum states of the propenyl radical at the energy $E = E_{avail} - E_{CN}$ (v, J). The vibrational frequencies and rotational constants of the propenyl radical were obtained by the same ab initio calculations, and the number of vibrational states was directly counted. In this calculation, the rotational energy of the propenyl radical was neglected, since the rotational energies are small compared to the vibrational energy. The calculated rotational distribution and the average rotational energy in CN (9.4 kJ/mol) from methacrylonitrile do not fit the experimentally measured distribution (Figure 6), implying different dissociation pathways. Similar calculations were performed for 2-butenenitrile, and the obtained rotational distribution does not fit to the experimentally measured distribution either (Table 1).

As an alternative, the dissociation into CN and the more stable allyl radical has been assumed. In fact, the allyl + CN channel from 2-butenenitrile was first suggested by North et al.[10] They successfully modeled the experimentally measured translational energy distributions assuming the allyl radical instead of the propenyl radical product. The dissociation energies and thus the available energies were obtained from the similar ab initio calculations for the allyl + CN channel from both 2-butenenitrile
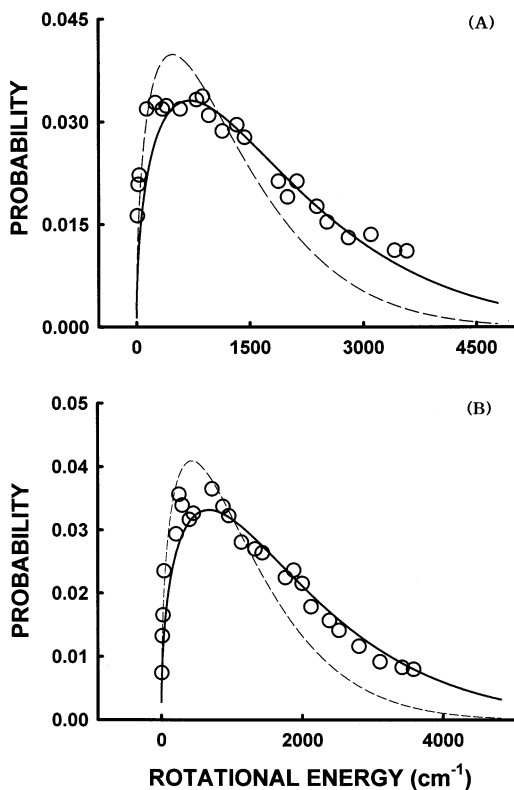
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Figure 6. Rotational population distributions of CN in the $v'' = 0$ level measured from the experiment (circles) and from the statistical prior calculations (solid line, allyl + CN channel; dashed line, propenyl + CN channel) for (A) 2-butenenitrile and (B) methacrylonitrile.

and methacrylonitrile at 193 nm. The available energies at 193 nm are, then, 169 kJ/mol for the allyl + CN radial channel from methacrylonitrile and 170 kJ/mol from 2-butenenitrile, respectively. Assuming the allyl + CN radical products, the calculated rotational energy distributions and average rotational energies agree better with the experimentally measured distribution than those for the propenyl + CN channel (Figure 6 and Table 1). In addition, the measured average translational energy release, 34.5 ± 4.5 kJ/mol, fits well the calculated value using the same

prior model assuming the allyl radical (28.4 kJ/mol) rather than the propenyl radical product (17.8 kJ/mol).

In the course of calculations for methacrylonitrile, that is, the calculation of the potential energies along the intrinsic reaction coordinates, it has been found that an H atom could migrate from the methyl group to the central carbon atom, forming an allyl type intermediate with a local minimum energy of 299 kJ/mol (Figure 7). In this calculation, the transition state geometry was optimized at the MP2 level and the single point energy was obtained by the B3LYP calculations using the 6-311+G (2df, 3pd) basis set. The transition state for the isomerization was found as the H atom bridged between the central and the terminal carbons with an energy barrier of 427 kJ/mol. This kind of isomerization has recently been suggested in the dissociation of 2-butenenitrile as well by North and co-workers.[10] The H and CN migrations are also expected in the dissociation of acrylonitrile, but mainly producing the molecular elimination products.[21]

However, it has been found that there is another isomerization path via CN migration followed by H migration (Figure 7). The CN group can migrate to the terminal ethylenic carbon followed by the H atom from the methyl group migrating to the central carbon, and as a result, stable allyl cyanide can be formed, from which CN elimination takes place. The transition state geometry for the CN migration was again optimized by the similar ab initio calculation, and the energy barrier was calculated. The calculated barrier is 345 kJ/mol, which is lower than that for the previously mentioned H migration channel. Then, with the calculated transition state geometries and the vibrational frequencies, the rate constants for both isomerization channels were calculated using the RRKM theory. The calculated rate constants are 3.7×10^7/s and 1.3×10^6/s for the CN and H migration channels, respectively. Thus, it is believed that the two channels may compete, but it is more probable that the elimination of CN occurs from allyl cyanide formed by the CN and subsequent H migrations.

Conclusion

The photodissociation of methacrylonitrile and 2-butenenitrile at 193 nm statistically occurs from the ground electronic state after internal conversion from the initial $\pi \rightarrow \pi^*$ transition.
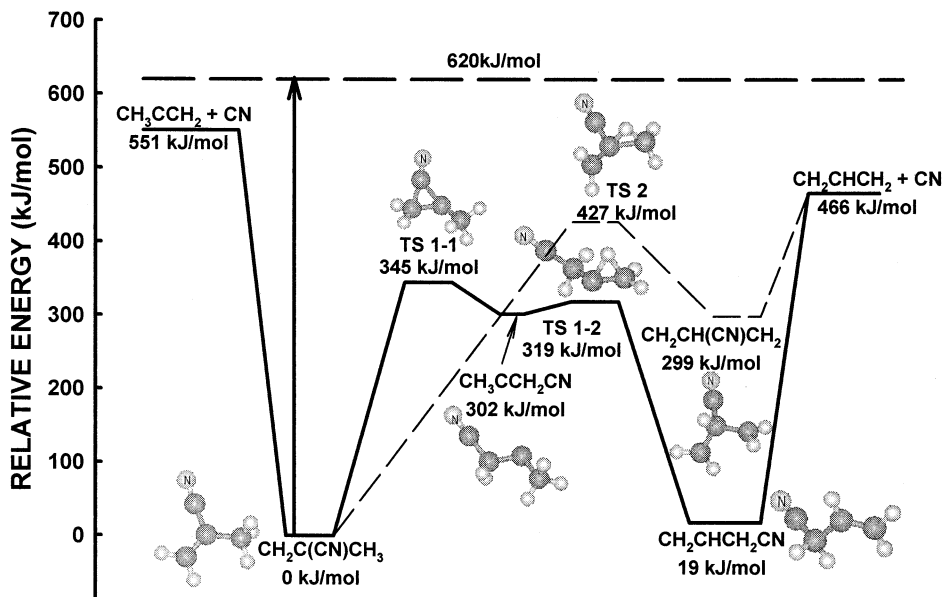

Figure 7. Schematic energy level diagram showing three different reaction paths obtained by ab initio calculations. The vertical arrow represents the photon energy in this experiment.

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Methacrylonitrile is isomerized to stable allyl cyanide by CN and H atom migration and dissociates into the CN and allyl radicals.

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