

Photodissociation Dynamics of *tert*-Butyl Isocyanide at 193 nm

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Photodissociation dynamics of *tert*-butyl isocyanide at 193 nm has been investigated by measuring rotationally resolved laser induced fluorescence spectra of CN fragments that were exclusively produced in the ground electronic state. From the spectra, internal energies of CN and translational energy releases in the products were obtained. The dissociation takes place in the excited triplet states which are strongly repulsive along the dissociation coordinate via curve crossing from the initially prepared state.

Key Words : Photodissociation, *t*-Butyl isocyanide, Triplet state

Introduction

Alkyl cyanides (R-CN) are more stable than alkyl isocyanides (R-NC) by some 20 kcal/mol and thus kinetics and mechanisms of isomerization of isocyanides to cyanides in the ground electronic state have extensively been studied.¹ However, studies of photodissociation dynamics of these molecules are rather sparse. Photodissociation of CH₃CN and CH₃NC was investigated by Simons and Ashfold in the vacuum ultraviolet region using various atomic resonance lamps where vibration and rotational energy distributions in the CN fragments were measured from emission spectra of CN in the B state.² The measured energy distribution was well explained by statistical theories invoking energy and angular momentum conservation constraints assuming long-lived intermediates. The excited states responsible for dissociation were identified as the 3p and 3s Rydberg states that are linear for both molecules. For CH₃NC, however, measured rotational population distribution particularly showed a distinct shape at 147 nm, where absorption to the excited state has in part bent π^* character.

Recently, photodissociation of cyclohexyl cyanide and cyclohexyl isocyanide at 193 nm was investigated both generating CN(X) and cyclohexyl radicals as products.³ Measured energy partitioning among products suggested that the dissociation takes place along the excited triplet surface via curve crossing from the initially prepared state for both molecules. In the case of aryl cyanides, Bersohn and coworkers studied the photodissociation of phenyl cyanide and phenyl isocyanide at 193 nm.⁴ The internal and translational energies of CN measured from laser induced fluorescence spectra and time-of-flight mass spectrometry showed almost the same for both molecules. It was again suggested that the dissociation occurs on a localized triplet surface via curve crossing from the initially excited state.

In this report, photodissociation of *tert*-butyl isocyanide was investigated by measuring rotationally resolved laser induced fluorescence spectra of the CN fragments. Vibrational and rotational population distributions in CN were measured

as well as translational energy releases from analyses of Doppler profiles in the spectra. The detailed dissociation dynamics were discussed from these experimental measurements.

Experiments

The experiments were performed in a flow cell with conventional pump-probe geometry. The cell was evacuated at a pressure of 10^{-3} Torr with a mechanical pump and vapor of the sample at ambient temperature was slowly flowed through the cell at a pressure of about 50 mTorr whose pressure was controlled by needle valves. The stated purity of 99% liquid *tert*-butyl isocyanide was purchased from Aldrich and used without further purification.

The photolysis light at 193 nm was an output of an ArF excimer laser (LEXTRA 50, Lambda Physik), which was unpolarized. The photolysis light beam was shaped as a circle (~5 mm dia. and ~10 mJ/cm²) with baffles inside arms attached to the cell. The baffles also minimized the scattered radiation into the detector. The probe light to measure laser induced fluorescence spectra of CN at 389-382 nm employing B \leftarrow X transition was an output of a dye laser (HD 500, Lumonics) pumped by the third harmonic of an Nd:YAG laser (YM-800, Lumonics). The probe light was collinearly counterpropagated to the photolysis laser beam. The power of the probe light was kept as low as possible to avoid saturation in the spectra, which was typically 30 μ J/pulse (~5 mm dia.). The LIF signal vs. the photolysis laser power showed linear dependence up to 20 mJ/cm², which ensured one-photon dissociation at the typical power used.

The fluorescence signal was detected with a photomultiplier tube (1P28A, Hamamatsu) perpendicularly mounted relative to the laser beams through cut-off filters to reduce scattered radiation of the photolysis light. The measured signal was fed to boxcars and processed with a signal processor. The delay between the pump and probe, typically about 100 ns was controlled with a digital pulse and delay generator. The sample pressure of 50 mTorr and the 100 ns delay time should provide a collisionless condition. The measured fluorescence spectra were corrected with variation of the pump and probe laser powers and stored in a PC.

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Results

The LIF spectrum of CN (X, v, N) produced from photodissociation of *tert*-butyl isocyanide employing the $B \leftarrow X$ electronic transition is presented in Figure 1. In the spectrum, the P-branch bandheads of the 0-0 and 1-1 vibrational transitions were clearly observed and the assignments for the R-branch rotational transitions are given on top of the spectrum.⁵ The individual transitions would result from excitations of pairs of the spin doublets corresponding to $J = N \pm 1/2$. The rotational energy distribution was obtained from integrated intensities of the peaks corrected by appropriate line strength factors (Fig. 2).⁶ The peak of the distribution was observed for $v = 0$ at $N = 32 \pm 2$ and the average rotational energy in CN was thus obtained from the normalized distribution, which was 26.4 ± 1.6 kJ/mol. The average rotational energy in CN at $v = 1$ was also measured from the distribution, which is 19.7 ± 2.8 kJ/mol. The vibrational population ratio in CN was obtained from the integrated intensities corrected by the Franck-Condon factors,⁷ which is 0.80/0.20 for $v = 0/1$.

In order to measure translational energies of the fragments,

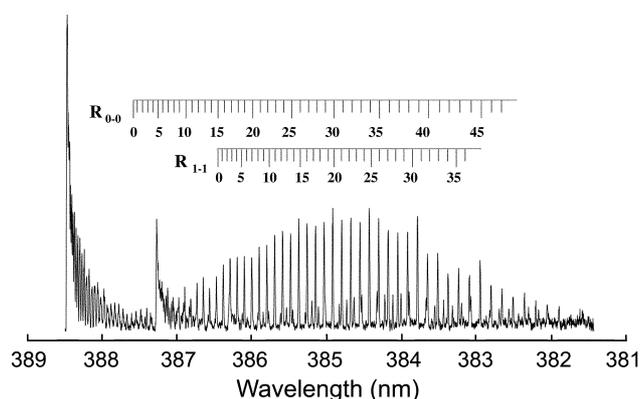


Figure 1. Laser induced fluorescence spectrum of CN produced from photodissociation of *tert*-butyl isocyanide at 193 nm employing the $B \leftarrow X$ electronic transition.

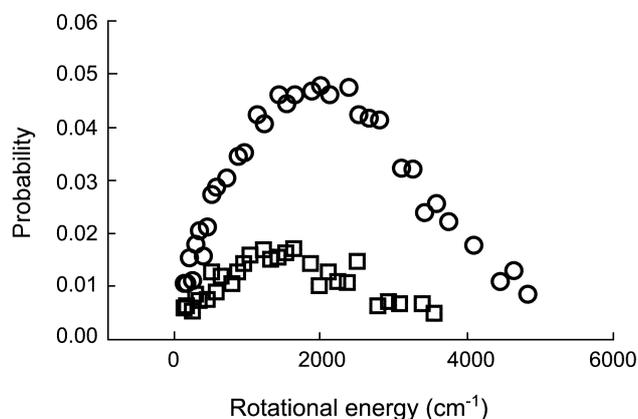


Figure 2. Rotational energy distribution of CN measured from the spectrum obtained in Figure 1. The open circles and squares represent the rotational distributions of CN in $v = 0$ and $v = 1$ vibrational states, respectively.

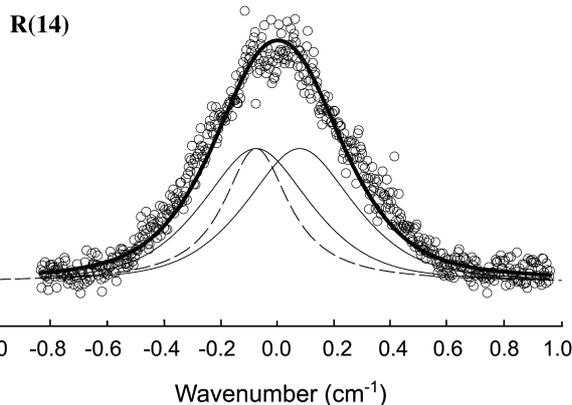


Figure 3. Doppler profile of the $N = 14$, R-branch rotational transition. The circles are the measured profiles. The thick solid line is a fit, from which the profiles resulting from the two overlapped transitions are estimated (thin solid lines). The dashed line is the laser line profile.

Doppler profiles of the individual transitions in the spectrum were analyzed. The laser line profile was first measured from the rotational line profile after translational relaxation by collisions, from which the estimated FWHM of the Lorentzian laser line profile was 0.27 cm^{-1} . In Figure 3, the Doppler broadened spectrum for $N = 14$ in the R-branch transitions is presented. The measured profile resulting from the two transitions from the two spin doublet states was deconvoluted with the laser line profile and the average translational energy of CN was measured from the second moment of the profile. Then, the center of mass translational energy release in both products was calculated to be 129 ± 10 kJ/mol.

Discussion

The UV absorption spectrum of *tert*-butyl isocyanide shows continuous, increasing absorption starting from around 210 nm. According to quantum chemical calculations, the highest occupied molecular orbitals are $\pi_{\text{C=N}}$ for CH_3CN and a lone pair orbital on C for CH_3NC , respectively.⁸ In both cases, however, the lowest unoccupied molecular orbital is π^* and the lowest energy electronic transition excites the molecule to the π^* state where the equilibrium geometry is bent. Assuming the same lowest energy transition as CH_3NC , an electronic transition at 193 nm would lead the parent molecule to the π^* state from which the dissociation takes place.

In order to figure out the dissociation mechanism, consideration of spin correlation arguments is helpful. The dissociation products are *tert*-butyl and CN radicals both in the spin-doublet ground state. Since each of the product radicals has two spin states, there are only four possible spin states that correlate to the pair of ground state product radicals. One of them must be the ground state and the other three must be the three excited triplet states because the excited singlet state must correlate to either of the product radicals being in the electronically excited state. Therefore, the dissociation at

193 nm must take place either from the ground state or the excited triplet states.

In the case of dissociation from the ground state, the dissociation occurs in the vibrationally hot ground state following internal conversion from the initially excited state. In the hot ground state, fast intramolecular vibrational relaxation should take place resulting in statistical energy partitioning among all degrees of freedom of the products. Considering the available energy at 193 nm to be 224 kJ/mol calculated from the photon energy (619 kJ/mol) and the dissociation energy (395 kJ/mol),⁹ the internal energy in the *tert*-butyl radical is 68.6 kJ/mol. The measured internal energy in CN is then almost half of that in much larger *tert*-butyl radicals, which implies non-statistical energy partitioning. Another argument that is against the ground state dissociation is the dissociation rate. With 39 vibrational degrees of freedom in this molecule, the RRKM calculation with 395 kJ/mol bond energy and with 224 kJ/mol excess energy shows that it should take over seconds for the necessary energy to be accumulated in one bond to be broken. During this time, the vibrationally hot molecules should be thermally deactivated by collisions with walls and/or other molecules producing no detectable CN for the present experimental time scale.

The electronic excitation at 193 nm prepares the parent molecule in the excited singlet state and the dissociation of CN takes place from the triplet states via curve crossing, which are strongly repulsive along the dissociation coordinate resulting in large translational energy releases observed in the present experiment. One thing to be mentioned is the non-Boltzmann shape of the rotational distribution of CN (Figs. 1 and 2). Similar rotational distributions were observed for CN from the photodissociation of ClCN

and BrCN excited in the first UV absorption band.^{10,11} In this case, a prompt dissociation from the repulsive state well explained the distribution by application of the rotational reflection principle, from which the shape of the bending potential energy surfaces could be examined.¹² In the present case of *tert*-butyl isocyanide photodissociation, however, whether the same arguments can be applied or not, further studies such as theoretical investigation of the excited potential energy surfaces and photodissociation as a function of excitation energies would be helpful to understand the dissociation dynamics in more detail.

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