The Wavelength Dependence of the Rates of Internal Energy Redistribution during the Photodissociation of 3-Iodopyridine

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The heterocyclic aromatic molecule 3-iodopyridine (C_5H_4NI) is photodissociated and studied with stateselective photofragment translational spectroscopy at 266 nm and 304 nm. Angular, velocity, and translational energy distributions are obtained for the ground state $I(^{2}P_{3/2})$ and excited state $I^{*}(^{2}P_{1/2})$ photodissociated iodine atoms. For the I channel, both a fast and a slow recoil speed distribution are observed at both 266 nm and 304 nm, which result from parallel electronic transitions. The fast I and I* distributions are proposed to result from an excitation to the alkyl iodide-type ${}^{3}Q_{0}(n,\sigma^{*})$ repulsive state, in accordance with mechanisms proposed for the photodissociation of iodobenzene. The observed slow I distributions are suggested to arise from absorptions to pyridine π,π^* optical doorway states which are predissociated by mixing with the alkyl iodide-type n,σ^* repulsive states. At 266 nm, the observed large increase in the relative quantum yield of slow iodine relative to that observed for iodobenzene correlates with the fact that the magnitude of the molar extinction coefficient for the ${}^{1}L_{b}$ band of 3-iodopyridine is larger than that for the ${}^{1}L_{b}$ band of iodobenzene. Like iodobenzene, the widths of the translational energy distributions of fast I and I* exhibit strong excitation photon energy dependences, which suggests a direct correlation between the rate of energy redistribution, which is in competition with the prompt dissociation process, and the density of pyridine-type dark vibronic states. Assuming that the observed correlation between the recoil velocity and the anisotropy parameter for the slow dissociation channel of I results from rotational depolarization, we are able to estimate dissociation times and rates of internal energy redistribution. We find that the rate of internal energy redistribution (IER) for the indirect slow dissociation process in 3-iodopyridine at 304 nm is comparable to that observed previously in iodobenzene, while the rate of IER observed for 3-iodopyridine at 266 nm is significantly larger than that observed previously in iodobenzene. Internal energy redistribution in the fast and slow dissociation channels is discussed in terms of the density of states and the coupling between the optical doorway states and nearby dark states.

Introduction

The photodissociation of aromatic iodides provides an interesting problem. Unlike alkyl iodides, $^{1-9}$ in which the C–I bond is the only chromophore, aromatic iodides possess two chromophores: the C-I bond and the aromatic π electron system. Thus, if the proper photon energy is used for photolysis, one would expect there to be a competition for the absorption of the photon between the C-I bond and the aromatic system. Experiments by Bersohn's group¹⁰ suggest that the photolysis of aryl halides is the result of an indirect dissociation, as opposed to the direct dissociation which is observed in alkyl iodides.⁴⁻⁸ Recent results obtained in our laboratory for the photodissociation of iodobenzene at 218 nm and 266 nm,^{11a,b} and at 304 nm,^{11c-e} clearly show that iodobenzene undergoes both a prompt (direct) photodissociation as well as a slow (indirect) photodissociation. The prompt dissociation process produces both the ground state $I({}^{2}P_{3/2})$ and the spin-orbit excited state $I^{*}({}^{2}P_{1/2})$ iodine atoms with high recoil velocities and is attributed to an alkyl iodide-type excitation/dissociation process, i.e., excitation to the alkyl iodide-type ${}^{3}Q_{0}(n,\sigma^{*})$ repulsive state, which directly yields I*, followed by crossing to the ${}^{1}Q_{1}(n,\sigma^{*})$ state which

produces I. The slower photodissociation process results in the production of $I({}^{2}P_{3/2})$ with low recoil velocities and is attributed to excitation to a benzene-type π,π^{*} bound "optical doorway" state which is predissociated by an alkyl iodide-type n,σ^{*} repulsive state(s). It is proposed that the benzene-type ${}^{1}L_{b}(\pi,\pi^{*})$ state and a triplet π,π^{*} state(s) are responsible for the formation of slow I at 266 nm and 304 nm, respectively.

The alkyl iodide A band consists of three dipole-allowed (n,σ^*) repulsive electronic states:²⁹ the 3Q_1 , 3Q_0 and 1Q_1 , in order of increasing energy, with absorption maxima at about 300 nm $(\epsilon = 4 \text{ L/mol}\cdot\text{cm})$, 260 nm $(\epsilon = 300 \text{ L/mol}\cdot\text{cm})$, and 240 nm $(\epsilon = 70 \text{ L/mol}\cdot\text{cm})$, respectively. It is well known that transitions to the 3Q_1 and 1Q_1 states are of perpendicular polarization and result in the production of ground state $I({}^2P_{3/2})$ atoms, while absorption to the 3Q_0 state is a parallel polarized transition which corresponds to the spin—orbit excited state $I({}^2P_{1/2})$ formation channel.² However, it has been shown that excitation to the 3Q_0 state produces ground state iodine in some alkyl iodides due to curve-crossing with the 1Q_1 state.⁴⁻⁸

It has been argued that the electronic spectrum of iodobenzene in the 240 to 310 nm region arises from a superposition of the benzene ${}^{1}L_{b}(\pi,\pi^{*})$ bound state and the repulsive alkyl iodide A band.^{12,13} This feature seems to be consistent with the results of our recent photodissociation studies of iodobenzene.¹¹

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An obvious analog of iodobenzene is the heterocylcic aromatic molecule 3-iodopyridine. The presence of the nonbonding electrons of the nitrogen atom makes the electronic structure of pyridine more complicated than that of benzene; the density of vibronic states is certainly larger. In the near-UV region there are five singlet and triplet π,π^* states and four singlet and triplet n,π^* states in pyridine.¹⁴⁻¹⁶ Specifically, the n,π^* states are the ³B₁ ($\lambda_{max} = 302 \text{ nm}$), ¹B₁ ($\lambda_{max} = 279 \text{ nm}$), ³A₂ ($\lambda_{max} = 230 \text{ nm}$), and the ¹A₂ ($\lambda_{max} = 228 \text{ nm}$) states. The π,π^* states are the 1³A₁ ($\lambda_{max} = 302 \text{ nm}$), the nearly degenerate ³B₂ and 2³A₁ ($\lambda_{max} = 250 \text{ nm}$), the ¹B₂ ($\lambda_{max} = 248 \text{ nm}$), and the ¹A₁ ($\lambda_{max} = 194 \text{ nm}$) states.

The electronic absorption spectra of substituted pyridines¹⁷⁻²⁰ such as 3-iodopyridine exhibit a strong and a weak band in the 190 nm to 300 nm wavelength region. The stronger band has its maximum at 228 nm and is correlated with the ${}^{1}L_{a}(\pi,\pi^{*})$ band, which is of ${}^{1}A_{1}$ symmetry in pyridine.¹⁷⁻²⁰ The energy maximum of the weaker band occurs at 264 nm and is correlated with the ${}^{1}L_{b}(\pi,\pi^{*})$ band, which is of ${}^{1}B_{2}$ symmetry in pyridine.¹⁷ Furthermore, there is a tail on the ${}^{1}L_{b}$ band which extends past 300 nm and is weakly absorbing at 304 nm. This absorption is likely due to the absorption of the C-I bond. It has been shown²⁰ that halogenation of pyridine with fluorine, chlorine, and bromine at the 2 and 3 positions causes a red shift of the first pyridine singlet π, π^* transition, and a blue shift of the first pyridine n, π^* transition (strong blue shift for 2-halopyridines, weak blue shift for 3-halopyridines). Although the studies that showed these results²⁰ did not include the iodopyridines, it is expected that iodine substitution would have a similar effect on the electronic structure of pyridine since the electron repulsion strength of iodine is between that of fluorine and chlorine.16

In this experiment we state-selectively study the photodissociation of a heterocyclic aromatic iodide, 3-iodopyridine, at 304 nm and 266 nm. For simplicity, we will refer to the ground state and excited state of iodine as I and I*, respectively. The photodissociation reactions studied here are

$$C_5H_4NI + h\nu \rightarrow C_5H_4N + I(^2P_{3/2})$$
(1)

and

$$C_5H_4NI + h\nu \rightarrow C_5H_4N + I^*(^2P_{1/2})$$
(2)

where $h\nu$ is equal to 4.66 eV ($\lambda = 266$ nm) or 4.07 eV ($\lambda = 304$ nm).

One would expect there to be qualitative similarities between the results for 3-iodopyridine and iodobenzene¹¹ because both molecules are six-membered aromatic rings with an iodine substituent. However, there are distinct differences between the two molecules which would lead one to expect there to be some differences in the photodissociation dynamics as well. The obvious differences are that 3-iodopyridine is a heterocyclic aromatic molecule in which there is a nitrogen atom with a nonbonding pair of electrons, and that 3-iodopyridine is of lower symmetry than iodobenzene. Consequently, because of the energetically nearby n,π^* states, there is a higher density of vibronic levels in the 200-300 nm region in 3-iodopyridine than in iodobenzene. The lower symmetry results in the absorption cross section of the ${}^{1}L_{b}$ band of 3-iodopyridine being significantly larger than that of iodobenzene. In this experiment we find that both direct and indirect photodissociation processes occur in 3-iodopyridine at 266 nm and 304 nm, as observed for iodobenzene. However, in contrast to iodobenzene, the rate

of internal energy redistribution (IER) increases when the photodissociation wavelength is changed from 304 nm to 266 nm.

Experimental Section

Details of the experimental apparatus and methodology are described elsewhere.^{8,11} Briefly, a single-stage pulsed-acceleration TOF mass spectrometer is used in combination with a linearly polarized pulsed laser (~ 20 ns). Room temperature vapor of I_2 is used to calibrate the TOF apparatus.^{8,11} At room temperature, 3-iodopyridine (C5H4NI, Sapon Laboratories Division of Karl Industries) vapor is introduced by effusion into the ionization region of the apparatus. The measured pressure in this region is found to be 1.8×10^{-6} Torr. The 3-iodopyridine is photolyzed by the 266 nm pulse (30 μ J/pulse), while state-selective ionization of I (I^*) is achieved with the 304.67 nm (304.02 nm) pulse (10 μ J/pulse). The 266 nm light is the fourth harmonic generated from the 1064 nm fundamental wavelength of the YAG laser. The 304 nm light is generated by pumping a dye laser (sulfarhodamine 640) with the 532 nm second harmonic light of the YAG and frequency doubling the dye laser output.

For the two-color (266 nm photolysis) experiment, the photolysis and ionization beams counterpropagate and are spatially overlapped in the photolysis/photoionization region of the spectrometer. The ionization pulse is delayed 4 ns with respect to the photolysis pulse, and ionization of the iodine photofragments is achieved via two-photon resonance plus onephoton ionization. The photolysis and photoionization beams are spatially overlapped such that the iodine ion signal was maximized in the presence of both pulses. Furthermore, the photolysis and photoionization pulse energies are adjusted such that each pulse alone yielded a minimized iodine ion background signal. Single color background spectra are collected for each data file in order that the single-color contribution to the twocolor ion signal could be subtracted from the two-color spectrum. Additionally, laser polarizations parallel and perpendicular to the detection axis ($\alpha = 0^{\circ}$ and 90° , respectively) are used at each photolysis wavelength in order to obtain information about the angular dependence of the photodissociation process.

The experiment at 304 nm is a single-color, single-pulse experiment in which the dye laser is tuned to give either 304.67 nm or 304.02 nm light (30 μ J/pulse) to investigate the I and I* channels, respectively. Photodissociation and photoionization occur within the same laser pulse for the single-color experiments.

A field-free condition is maintained during a delay time τ of 1.50 μ s after the laser pulse. The state-selectively ionized iodine atoms are then accelerated up toward the detector by applying a pulsed acceleration voltage (approximately -1500 V with a pulse duration of 1.0 μ s) to the acceleration electrode. After traveling through a field-free drift region, the ions pass through a discrimination pinhole (6.0 mm diameter) and the TOF distribution is measured. The discrimination pinhole discriminates against photoions with large velocity components perpendicular to the detection axis (velocities in the x and y directions which are greater than 150 m/s).^{11e}

All gas phase and solution phase ultraviolet (UV) absorption spectra were taken on a Cary 219 spectrophotometer. The gas phase spectrum (Figure 1) was collected in the wavelength region of 200–350 nm using a 10 cm path-length cylindrical quartz cuvette and a spectral resolution of 1 nm. The solution phase spectra (in hexane) of 3-iodopyridine (2.47×10^{-4} M) and iodobenzene (2.49×10^{-4} M) were taken in 1 cm quartz cuvettes (see Figure 2).



Figure 1. Gas phase ultraviolet spectrum of 3-iodopyridine taken on a Cary 219 spectrometer and taken in a 10 cm cell. Because vapor pressure data for 3-iodopyridine are not available, it is not possible to calculate the molar extinction coefficient from the gas phase spectrum.



Figure 2. Ultraviolet absorption spectra of 3-iodopyridine (upper trace) compared with iodobenzene (lower trace) in the ${}^{1}L_{b}$ band region, taken in hexane in a 1 cm quartz cuvette. The concentrations are 2.47 \times 10⁻⁴ M for 3-iodopyridine and 2.49 \times 10⁻⁴ M for iodobenzene. At 266 nm, the values of the molar extinction coefficients for each molecule are found to be 2560 L/mol-cm for 3-iodopyridine and 570 L/mol-cm for iodobenzene.

Results

A. The I Photodissociation Channel. The lab velocity (v_z) distributions are presented as a and b in Figure 3 for the photodissociation of 3-iodopyridine at 304.67 nm and 266 nm, respectively. The velocity distribution for the I channel exhibits a relatively narrow high velocity peak and a broader low velocity



Figure 3. Lab velocity distribution for iodine ions in the *z*-direction for the $I(^{2}P_{3/2})$ channel following photodissociation of (a) 3-iodopyridine at 304.67 nm and (b) 3-iodopyridine at 266 nm. The upper trace in each figure is for photolysis with parallel polarized light, and the lower trace in each figure is for photolysis with perpendicular polarized light. The presence of high velocity and low velocity distributions in each figure indicates that multiple dissociation processes are occurring in the photodissociation of these molecules.

peak of comparable intensity for $\alpha = 0^{\circ}$. It is worth noting at this point that the slow velocity distribution which was previously observed for iodobenzene in our laboratory^{11c-e} is much lower in intensity than the observed fast distribution. The velocity distribution for $\alpha = 90^{\circ}$ also exhibits fast and slow velocity peaks. However, whereas the peak heights of the fast and slow velocity peaks are similar for $\alpha = 0^{\circ}$, for $\alpha = 90^{\circ}$ the intensity of the high velocity peak is much less than the slow velocity peak, indicating a strong parallel anisotropy of the high velocity peak.

Figure 4a shows the total translational energy distribution, $G(E_{\rm T})$, and the translational energy dependence of the anisotropy parameter, $\beta(E_{\rm T})$, for the photodissociation at 304 nm. These are obtained from the ν_z distributions by correcting for the velocity dependence of the detection solid angle and applying the conservation of momentum rule. Our results suggest that more than one dissociation process is occurring upon the absorption of a single photon. A quantitative indication of this is given by the anisotropy parameter β , which is related to the lifetime of the parent molecule in its excited state. From Figure 4a, it is clear that the photodissociation of 3-iodopyridine at 304 nm results from a parallel electronic transition, since β - $(E_{\rm T}) > 0$ throughout the spectrum, and its recoil velocity dependence is consistent with our dynamical interpretation based on the rate of internal energy redistribution and the dissociation time dependence of the anisotropy as will be discussed later. Furthermore, it is clear from translational energy distribution in Figure 4a that, as in iodobenzene,¹¹ there are at least two different dynamical processes occurring during the photodissociation of 3-iodopyridine at 304 nm, since there are two distinct distributions present in the spectrum. The higher translational energy distribution corresponds to the component of $\beta(E_{\rm T})$ which is independent of $E_{\rm T}$ (at the peak $\beta = 1.6$),



Figure 4. The high and low total translational energy distributions, $G_{h}(E_{T})$ and $G_{1}(E_{T})$, and the corresponding $\beta_{h}(E_{T})$ and $\beta_{1}(E_{T})$, for the photodissociation of (a) 3-iodopyridine at 304.67 nm and (b) 3-iodopyridine at 266 nm. In each case $\beta_{h}(E_{T})$ is independent of the translational energy while $\beta_{1}(E_{T})$ decreases smoothly as E_{T} decreases.

while the lower translational energy distribution corresponds to the component of $\beta(E_{\rm T})$ which is dependent on the recoil speed ($\beta = 0.1-1.2$).

From Figure 3b, it is clear that multiple dynamical processes are also occurring during the photodissociation of 3-iodopyridine at 266 nm for the I formation channel. Figure 4b presents $G(E_T)$ and $\beta(E_T)$ for the photodissociation of 3-iodopyridine at 266 nm. Clearly the dynamical processes which result in the photodissociation of 3-iodopyridine at 266 nm result from parallel electronic transitions. Also, as in the case of photodissociation at 304 nm, $G_n(E_T)$ corresponds with the component of $\beta(E_T)$ which is independent of E_t ($\beta_h(E_T) = 1.4$ at the peak), while $G_1(E_T)$ corresponds to the component of $\beta(E_T)$ which is dependent upon the translational energy ($\beta_1(E_T) = 0.2-0.8$).

The most striking feature of the translational energy distribution observed for 3-iodopyridine at both 304 nm and 266 nm is the dramatic increase in the intensity of $G_1(E_T)$ relative to G_h - $(E_{\rm T})$ (Figure 4), as compared to that observed for iodobenzene.¹¹ The relative quantum yield of the slow I increases from 0.30 for iodobenzene^{11e} to 0.50 for 3-iodopyridine at 304 nm. This increase is even more dramatic at 266 nm, i.e., from 0.13 for iodobenzene^{11a} to 0.56 for 3-iodopyridine at 266 nm. This is likely due to the fact that the molar extinction coefficient for the ${}^{1}L_{b}$ band of 3-iodopyridine, which is responsible for the formation of slow I at 266 nm, is larger than that for the ${}^{1}L_{b}$ band of iodobenzene (see Figure 2). Perhaps triplet excitation responsible for the slow I formation at 304 nm is also enhanced in 3-iodopyridine, compared to that in iodobenzene.^{11c-e} Table 1 summarizes the relevant parameters which describe photodissociation dynamics of 3-iodopyridine at 266 nm and 304.67 nm for the I formation channel.

B. The I* Photodissociation Channel. Table 2 summarizes the relevant parameters which describe the photodissociation dynamics at 304.02 nm and 266 nm for the I* formation channel of 3-iodopyridine. Figures 5a and 6a present the lab velocity distributions at $\alpha = 0^{\circ}$ and $\alpha = 90^{\circ}$, and the corresponding $G(E_T)$ and $\beta(E_T)$, respectively, for the formation of I* following the photodissociation of 3-iodopyridine at 304 nm. As was observed for the I* formation channel of iodobenzene at 304 nm,^{11b,c} the translational energy distribution $G(E_T)$ for the I* formation channel of 3-iodopyridine at 304 nm exhibits only a single, sharp peak, in contrast to the translational energy distribution for the I formation channel at 304 nm. Clearly, from Figure 6a, the formation of I* results from a parallel electronic transition. The relative yield of I^* , $F(I^*)$, for 3-iodopyridine at 304 nm is determined to be 0.006, in strong agreement with that for iodobenzene (0.005) determined at 304 nm.^{11c} The fact that the value of the anisotropy parameter is large ($\beta = 1.5$) and independent of the translational energy release evidences that I* formation in 3-iodopyridine, as in iodobenzene,^{11e} results from a prompt dissociation which follows photoexcitation to the alkyl iodide ${}^{3}Q_{0}(n,\sigma^{*})$ electronic state.

Figures 5b and 6b presents the lab velocity distributions at $\alpha = 0^{\circ}$ and $\alpha = 90^{\circ}$, and the corresponding $G(E_{\rm T})$ and $\beta(E_{\rm T})$ for the formation of I* following the excitation of 3-iodopyridine at 266 nm. Again, from the large value of the anisotropy parameter^{21a} ($\beta = 1.6$ at the peak), it is evident that I* formation from 3-iodopyridine results from a parallel photodissociation process due to excitation to the ${}^{3}Q_{0}(n,\sigma^{*})$ state. We observe

TABLE 1:	Summary of	of the Photodiss	ociation Dynam	ics of 3-Iodopyridin	e for the I	(² P _{3/2}) Photo	odissociation (Channels at 266
nm and 304	nm ^a		-					

λ (nm)	relative quantum yield	$\langle E_{ m avl} angle$	$\langle E_{\mathfrak{l}} \rangle$	$\langle E_{ m int} angle$	$\langle E_{\rm int} \rangle / \langle E_{\rm avl} \rangle$	fwhm of $G(E_t)$	β	<i>t</i> (ps)	$-\mathrm{d}E_{\mathrm{t}}/\mathrm{d}t$
266 fast	0.42	46.4	27.5 ± 0.4	18.9	0.41	15.7 ± 0.9	1.4 ^b	0.53	20
304 fast	0.36	40.4	9.3 ± 0.2 25.2 ± 0.3	57.1	0.80	10.7 ± 0.4 8.4 ± 0.9	1.6	0.78-1.45	39
slow	0.50	32.7	8.7 ± 0.4	24.0	0.73	10.4 ± 0.2	1.0 - 0.1	0.54-1.66	22

^{*a*} Energies are in kcal/mol; the rates of IER ($-dE_t/dt$) are in kcal/mol-ps. ^{*b*} If the fast I channel at 266 nm is taken to result from a mixed parallel/perpendicular transition, then $\beta_{\parallel} = 1.6$ which corresponds to a dissociation time of 0.36 ps.

TABLE 2: Summary of the Photodissociation Dynamics of 3-Iodopyridine for the $I(^{2}P_{1/2})$ Photodissociation Channel at 266 nm and 304 nm^a

λ (nm)	relative quantum yield	$\langle E_{\rm avl} \rangle$	$\langle E_{\rm t} \rangle$	$\langle E_{ m int} angle$	$\langle E_{\rm int} \rangle / \langle E_{\rm avl} \rangle$	fwhm of $G(E_t)$	β	<i>t</i> (ps)
266	0.022	24.7	15.1 ± 0.2	9.6	0.39	12 ± 2	1.6	0.36
304	0.006	11.2	9.5 ± 0.6	1.7	0.15	6.8 ± 0.6	1.5	0.42

^a Energies are in kcal/mol.



Figure 5. Lab velocity distribution in the *z*-direction for the iodine fragments formed from the $I^{(2P_{1/2})}$ channel following photodissociation of (a) 3-iodopyridine at 304.02 nm and (b) 3-iodopyridine at 266 nm. The upper trace in each figure is for photolysis with parallel polarized light, and the lower trace is for perpendicular polarized light.



Figure 6. Total translational energy release distributions $G(E_T)$ and the anisotropy parameters as a function of translational energy, $\beta(E_T)$, for the photodissociation of (a) 3-iodopyridine at 304.02 nm and (b) 3-iodopyridine at 266 nm.

that the relative yield of I* at 266 nm is 0.022, which is three to four times larger than that observed at 304 nm. However, this is still an order of magnitude lower than that observed for the I* channel of iodobenzene at 266 nm.^{11a} Furthermore, the full width at half-maximum (fwhm) of the translational energy distribution for the 266 nm I* channel of 3-iodopyridine (12 kcal/mol) is nearly twice that observed for the I* channel at 304 nm, and nearly 4 kcal/mol larger than the fwhm observed for the I* channel of iodobenzene at 266 nm.^{11a} These last two observations indicate that coupling between the alkyl iodide repulsive optical doorway state and the pyridine vibronic states strongly influences the dynamics observed in the I* channels.

C. Time Dependence of the Anisotropy Parameter and the Rate of Internal Energy Redistribution. The correlation between recoil velocity and spatial distributions (anisotropy parameter) of the photodissociating fragments could result from a number of reasons.^{21b} Two of these are: (1) dynamical processes in the excited state with lifetimes comparable with those for dissociation could change the dissociation direction of the detected iodine atoms during the dissociation process. e.g., molecular bending or molecular rotation processes in the excited state; (2) if the excited state has different angular disposition of the dissociated atoms with respect to the direction of the photoexcitation transition moment, the absorption process from hot bending vibrations could produce an excited state with different angular distribution as given by the Franck-Condon factors involved. If the molecule dissociates rapidly, molecules with different bent geometries in a given excited state produce fragments with a different rotational excitation (and thus with correspondingly different recoil velocities) as well as different spatial distribution.

In case 1, the changes in the anisotropy parameter with recoil velocity can yield information regarding the rate of energy redistribution. Case 2, however, does not yield any time dependent information. Since our experiments are room temperature studies, the population of C-C-I vibrational modes is possible. The n,σ^* excitation most likely changes the C-I bond distance, and the π,π^* excitation slightly expands the aromatic ring. Neither excitation is expected to change the C-Iangular configuration with respect to the ring. On the other hand, n,π^* excitation changes the hybridization of, and thus the geometry around, the nitrogen atom. However, the C-I bond is too far away from the nitrogen atom for the n,π^* excitation to change the angle around the carbon atom to which the iodine atom is attached. These facts might allow us to assume that the observed changes in the anisotropy factor are due to molecular rotation rather than to bending geometry changes in the excited state, or from absorption from excited bending vibrations. In molecules like I-CN, one cannot make this assumption safely. Making the above assumption, we were able to determine the dissociation times for the I photodissociation channels from the observed recoil speed dependence of the anisotropy parameter. These are summarized in Table 1. In this case, the anisotropy parameter β contains information about the dissociation time and the excited state lifetime of a dissociating molecule. It has been shown^{22,23} that for a symmetric top molecule with its figure axis coinciding with the dissociation axis, the value of the anistotropy parameter at some time t after photoexcitation, $\beta(t)$, is related to the initial value $\beta_0 = 2$ (owing to depolarization effects in our apparatus, $\beta_0 =$ $(1.8)^{11c-e}$ at time zero by a rotational correlation function:

$$\beta(t) = \beta_0 \langle D_{00}^2(t) \rangle \tag{3}$$

The brackets denote an average over the rotational ensemble. This average depends on the temperature T and the asymmetry parameter $b = (I - I_z)/I_z$, where I is the perpendicular moment of inertia and I_z is the moment of inertia about the symmetric top figure axis. As with iodobenzene,^{10,11} 3-iodopyridine is treated as an approximate symmetric top molecule since the figure axis closely coincides with the C–I bond, and the two moments of inertia about the C–I bond are approximately equal.



Figure 7. Rotational correlation function for 3-iodopyridine as a function of the reduced time, t^* . The reduced time is the dissociation time, *t*, divided by the molecular rotational time, t/τ_r . For 3-iodopyridine $\tau_r = 1.76$ ps at 298 K.

Figure 7 shows the rotational correlation function as a function of reduced time t^* . The reduced time is related to the dissociation time t by

$$t^* = t(I/kT)^{-1/2}$$
(4)

where the quantity $(I/kT)^{1/2}$ is the rotation time of the molecule (1.76 ps for 3-iodopyridine). Thus, from our knowledge of the velocity dependence of the anisotropy parameter, we are able to estimate dissociation times for the direct and indirect processes. Dissociation times are presented in Table 1 for the fast and and slow I channels and in Table 2 for the I* channel.

The time dependence of the anisotropy parameter also allows us to study the time dependence of the translational energy release for the indirect dissociation process. Since $\beta(E_{\rm T})$ and $\beta(t)$ are known, it is relatively simple to arrive at $E_T(t)$, where $E_{\rm T}(t)$ is the translational energy release as a function of time. a and b in Figure 8 present the time dependence of the translational energy release for the indirect photodissociation processes at 304 nm and 266 nm, respectively. The slope in each figure, dE_T/dt , is approximately linear and represents the rate of internal energy redistribution (IER) into the pyridine ring following the initial electronic excitation. We find that the rate of IER to be $-(dE_T/dt) = 22$ kcal/mol·ps at 304 nm and 39 kcal/mol·ps at 266 nm. While the rate of IER observed here at 304 nm is comparable to that observed in iodobenzene^{11c-e} (23 kcal/mol·ps), the rate of IER observed here at 266 nm is greater than that observed in iodobenzene^{11c-e} (15 kcal/mol·ps).

D. Energy Partitioning. Upon photodissociation, excess energy is made available to the system for redistribution into translational and internal energy modes. The excess available energy is given by the energy conservation relationships for I and I* respectively:

 $\langle E_{\rm av1} \rangle = h\nu - D_0^0 + E_{\rm int}^{\rm p} = \langle E_{\rm t} \rangle + \langle E_{\rm int} \rangle$

$$\langle E^*_{\rm avl} \rangle = \langle E_{\rm avl} \rangle - E_{\rm s.o.} \tag{6}$$

where $h\nu$ is the photolysis photon energy, D_0^0 is the C–I dissociation energy, E_{int}^p is the internal energy of the parent molecule, $\langle E_{int} \rangle$ is the internal energy of the photofragments, $\langle E_t \rangle$ is the total translational energy released upon photodissociation, and $E_{s.o.} = 21.7$ kcal/mol is the I* spin-orbit coupling energy. Reasonable estimates for the C–I bond dissociation



Figure 8. Total translational energy release as a function of time for the low energy I distribution for the (a) photodissociation of 3-iodopyridine at 304.67 nm and (b) photodissociation of 3-iodopyridine at 266 nm. The slope in each figure, dE_T/dt , represents the rate of internal energy redistribution following excitation. These rates are found to be 39 kcal/mol-ps for 3-iodopyridine at 266 nm and 22 kcal/mol-ps for 3-iodopyridine at 304.67 nm.

energy and the parent molecule internal energy for 3-iodopyridine are the values used for iodobenzene.^{11c-e} Thus we use the values $D_0^0 = 63.9$ kcal/mol for the C-I bond dissociation energy and $E_{int}^p = 2.8$ kcal/mol.

From Figure 9, it is clear that the internal energies of the pyridine radical photofragments formed from the production of fast I and I* are strongly dependent on the photon energy or, equivalently, on $\langle E_{avl} \rangle$, which is much like the behavior observed in iodobenzene¹¹ and CF₃I.^{8c,24} Furthermore, the fwhm's observed for both rapid dissociation channels show a strong dependence on $\langle E_{avl} \rangle$ (Figure 10). These results indicate that pyridine vibrational modes are strongly coupled to the carbon—iodine bond dissociation coordinate as discussed for iodobenzene¹¹ and CF₃I.^{8c,24} These observations further indicate that the rates of energy redistribution in the fast channels are correlated with the amount of excess energy, and thus with the density of vibronic states, as was proposed previously for iodobenzene.^{11a,b}

Discussion

(5)

A. The Dynamics of the Electronic Excitation at 304 nm. As with iodobenzene,¹¹ the photodissociation process which corresponds to the higher translational energy distribution is undoubtedly a result of a direct dissociation along the C–I bond. This is analogous to what is observed in the alkyl iodides⁴⁻⁸ in which the C–I bond is electronically excited from its ground state to a repulsive potential energy surface which results in a direct dissociation. In the alkyl iodides this involves the excitation of a nonbonding $5p\pi$ valence electron on the iodine atom to an antibonding σ^* orbital on the C–I bond.² The fact that the value of the anisotropy parameter ($\beta = 1.6$), which corresponds to the higher translational energy distribution of I, is close to the limiting value of 2 for a parallel transition, and the fact that this value of β is independent of the translational



Figure 9. Plot of the photon energy dependence of (a) the internal energy of the pyridinyl radical following photodissociation of 3-iodopyridine at 304 nm and 266 nm and, for comparison, (b) the internal energy of the CF₃ radical following the photodissociation of CF₃I at 248 nm and 304 nm. The internal energy for the CF₃ radical at 304 nm is taken from ref 8c, while the internal energy of the CF₃ radical at 248 nm is taken from ref 23. The internal energy for the phenyl radical at 304 nm is taken from ref 11. The solid circles are for the fast I channel, and the open circles are for the I* channel. Note that the slopes of 0.83 and 0.59 determined for the curves of the pyridine radical fast I and I* channels, respectively, are larger than the those for the CF₃ radical (0.57 for I, 0.56 for I*) that represents a strongly coupled case. This strong photon energy dependence of the internal energy of the pyridinyl radical indicates that, in analogy with the photodissociation of CF₃I, vibrational modes of the pyridinyl radical are strongly coupled to the dissociation along the carbon-iodine coordinate.

energy release indicate that this prompt dissociation results from excitation to the alkyl iodide ${}^{3}Q_{0}(n,\sigma^{*})$ state followed by efficient curve-crossing to the ${}^{1}Q_{1}(n,\sigma^{*})$ state to produce I.

In further accordance with the results observed for the photodissociation of iodobenzene at 304 nm,^{11c-e} the relative yield of I* is quite low (0.006 as compared to 0.005 for iodobenzene at 304 nm.^{11c} Also, the fact that the value of the anisotropy parameter for the I* photodissociation channel of 3-iodopyridine is large ($\beta = 1.5$) and independent of the translational energy release strongly indicates that I* production results from excitation to the repulsive ${}^{3}Q_{0}(n,\sigma^{*})$ alkyl iodide state followed by dissociation from the same repulsive surface.

As has been observed for the photodissociation of iodobenzene at 304 nm,^{11c} the overall translational energy distribution obtained for the I photodissociation channel of 3-iodopyridine at 304 nm exhibits a lower translational energy distribution as well as the higher translational energy distribution discussed previously (see Figure 4a). This distribution, as with iodobenzene,¹¹ arises from a parallel electronic transition since the value of the anisotropy parameter is always greater than zero. Furthermore, this distribution corresponds to an anisotropy parameter which is dependent on the photofragment recoil velocity and thus the translational energy release ($\beta = 0.1 -$ 1.2). This observed correlation between the photofragment recoil velocity and β indicates that a process other than direct dissociation from a repulsive n,σ^* state occurs. As stated previously, 10a, 11c-e, 22, 23 the photodissociation lifetime t is in direct one-to-one correspondence with the anisotropy parameter β . The



Figure 10. Plot of the full width at half-maximum (fwhm) versus the excess available energy for the fast I channel (triangles) and the I* channel (circles) for 3-iodopyridine. Corresponding plots from ref 11b for iodobenzene are presented for comparison (fast I = long-dashedline, $I^* =$ short-dashed line). The strong dependence of the fwhm on the excess available energy indicates that internal energy redistribution for both the fast I and I* channels of 3-iodopyridine becomes more efficient with increasing photon energy owing to stronger coupling of the alkyl iodide optical doorway repulsive states with the pyridinetype bound vibronic dark states which are increasing in density as the energy increases. Further evidence of the IER efficiency increasing with the density of vibronic states is given by the fact that the slopes of the 3-iodopyridine plots are both larger than those of the iodobenzene plots, suggesting the IER rates in the fast I and I* channels are increasing more rapidly with energy than are the IER rates of iodobenzene.

smaller β is, the longer the dissociation lifetime is. The fact that we observe β decreasing with the recoil velocity (or, equivalently, translational energy) means that photofragments with lower recoil velocities are produced from molecules with longer dissociation lifetimes. We, in fact, observe a *range* of lifetimes in the low E_T distribution. As t increases and approaches the molecular rotation time τ_r , more energy is redistributed and more molecular rotation takes place prior to photodissociation; i.e., energy redistribution competes with dissociation. This is consistent with predissociation.

A mechanism for the photodissociation of iodobenzene at 304 nm has been proposed in which a benzene-type triplet π,π^* state and the alkyl iodide ${}^{3}Q_{0}(n,\sigma^{*})$ state are both excited in competition with each other, resulting in the observed low and high translational energy distributions.^{11c-e} In this model, the bound π,π^* state is predissociated by an alkyl iodide-type repulsive state(s), resulting in the production of the slow I photofragments. A similar process may occur when 3-iodopyridine is photodissociated at 304 nm. In the 300 nm region, pyridine has both a triplet, π,π^* state and a triplet n,π^* state. Electron paramagnetic resonance data²⁵ indicate that these states are the ${}^{3}A_{1}(\pi,\pi^{*})$ state and the ${}^{3}B_{1}(n,\pi^{*})$ state. Substitution of an iodine atom in the 3 position on the pyridine ring would shift ${}^{3}A_{1}(\pi,\pi^{*})$ to a lower energy and likely shift ${}^{3}B_{1}(n,\pi^{*})$ to a slightly higher energy, as has been observed in the other 3-halopyridines.²⁰ For 3-iodopyridine these states will be referred to as the $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$ states. The question then is whether it is excitation to $T_1(\pi,\pi^*)$ or $T_2(n,\pi^*)$ which produces predissociated I.

The large intensity of the slow I distribution observed at 304 nm, compared to that observed for the photodissociation of iodobenzene¹¹ at 304 nm, suggests that it is the $T_1(\pi,\pi^*)$ pyridine state which is excited. The $T_1 \leftarrow S_0$ transition in pyridine in the 300-320 nm region is well known to be exceptionally weak.²⁶⁻²⁸ In fact, Japar and Ramsay²⁶ needed

a path length of about 2000 m to observe the singlet-triplet transition in pyridine using UV absorption spectroscopy. However, the substitution of an iodine atom onto the pyridine ring ought to enhance the intensity of the lowest singlet-triplet transition somewhat since the $C_{2\nu}$ symmetry of pyridine is broken. In addition, this enhancement might also result from vibronic mixing of a ${}^{3}A_{1}(\pi,\pi^{*})$ charge transfer state (which results from the mixing of iodine p_{π} electrons with pyridine π electrons) with the pyridine ${}^{3}A_{1}(\pi,\pi^{*})$ state, which is consistent with the observed parallel polarization of the slow I distribution. Also, the oscillator strengths of n,π^* states are known to be considerably weaker than those of π,π^* states. Therefore, we propose that the optical doorway state which results in the production of slow I is the triplet $T_1(\pi,\pi^*)$ state of 3-iodopyridine, which arises from the mixing of the ${}^{3}A_{1}(\pi,\pi^{*})$ charge transfer state and the pyridine ${}^{3}A_{1}(\pi,\pi^{*})$ state.

Production of I via the indirect channel must then result from predissociation of the initially excited pyridine type bound state by a repulsive alkyl iodide-type n,σ^* state(s). The mechanisms proposed for the photodissociation of 3-iodopyridine at 304 nm can now be written as

$$^{1}A_{1} \xrightarrow{h_{\nu}} {}^{3}Q_{0}(n,\sigma^{*}) \xrightarrow{I^{*}(fast)} I^{*}(fast)$$

$$\downarrow^{fast} {}^{1}Q_{1}(n,\sigma^{*}) \xrightarrow{I}(fast)$$

$$^{1}A_{1} \xrightarrow{h_{\nu}} T_{1}(\pi,\pi^{*}) \xrightarrow{3 \text{ or } 1}(n,\sigma^{*}) \xrightarrow{I}(slow)$$

B. The Dynamics of the Electronic Excitation at 266 nm. The fast I photodissociation channel of 3-iodopyridine observed following excitation at 266 nm is also quite similar to that observed in iodobenzene at 266 nm.^{11a,b} This channel clearly results from a parallel transition ($\beta = 1.4$). The value of β is independent of the translational energy release, which is the same as what is observed for the photodissociation of iodobenzene at 266 nm,^{11a,b} and is lower than the value of $\beta = 1.6$ observed for the fast I channel of 3-iodopyridine at 304 nm. Furthermore, it is observed that, as in iodobenzene,¹¹ the fwhm of the high energy distribution nearly doubles as the excess available energy is increased upon going from 304 nm to 266 nm (Figure 10). It has been proposed^{11a,b} that the production of fast ground state iodine in iodobenzene at 266 nm results from an excitation to the alkyl iodide repulsive ${}^{3}Q_{0}(n,\sigma^{*})$ optical doorway state which is strongly coupled to benzene π,π^* dark states, followed by crossing to the ${}^{1}Q_{1}(n,\sigma^{*})$ state to produce fast I.

The observation for the fast I channel that the value of $\beta =$ 1.4 at 266 nm is lower than the value of $\beta = 1.6$ at 304 nm is similar to the observation made for iodobenzene^{11a,b} at 266 nm $(\beta = 1.2)$. For iodobenzene^{11a,b} it was discussed that for a dissociation from purely repulsive state, as in CH₃I,^{5-8,10a} the value of β should be close to its limiting value (+2 for a parallel transition, -1 for a perpendicular transition). Also, the value of β would likely increase as the average fragment velocity increases, if the dissociation dynamics are the same at the different excitation wavelengths. As has been discussed previously,^{11e} this is due to the fact that the parent molecule velocity tends to reduce the value of the anisotropy parameter at lower fragment velocities. The decrease in the value of β for the fast I channel might therefore indicate that the production of fast I results from an initial excitation to the repulsive ${}^{3}Q_{0}$ - (n,σ^*) alkyl iodide optical doorway state which is in turn more strongly coupled to a pyridine bound state(s) than at 304 nm, resulting in a longer dissociative lifetime. However, if coupling

or mixing of the dissociative n,σ^* optical doorway state with pyridine π,π^* and/or n,π^* vibronic states increases the dissociative lifetime (lower β), then we ought to observe a *lower* β in 3-iodopyridine than in iodobenzene for this fast I channel owing to the larger density of vibronic states in 3-iodopyridine. Moreover, if this would have been the case, we would have observed a similar lower value of β for the I* channel at 266 nm, as opposed to our results, since I* is also produced from the same ${}^{3}Q_{0}$ state.

The lower value of β observed for the fast I channel at 266 nm is consistent with an electronic transition which has both a parallel and a perpendicular polarization component. The MCD experiments of Gedanken and Rowe9a resolved the alkyl iodide A-band into its three optically allowed components, with the percent contribution of each component to the overall A-band intensity varying with wavelength. Further experiments by Gedanken^{9b} demonstrated that the intensity contribution by each component n,σ^* state also varies with the type of alkyl group bonded to the iodine atom. Hwang and El-Sayed^{8b,c} used stateselective photofragment translational spectroscopy to show that production of $I({}^{2}P_{3/2})$ in C₂F₅I and CF₃I at 304 nm results from mixed electronic transitions to the parallel ${}^{3}Q_{0}(n,\sigma^{*})$ state and the perpendicular ${}^{3}Q_{1}(n,\sigma^{*})$ state, with relative contributions from each state being consistent with the MCD results of Gedanken et al.⁹ for C_2F_5I and CF_3I . The fractions of each polarization, X_{\parallel} and X_{\perp} for parallel and perpendicular, respectively, can be determined from

$$\beta = X_{\parallel}\beta_{\parallel} - X_{\perp}\beta_{\perp} \tag{7}$$

where $\beta_{\parallel} = 1.8$ and $\beta_{\perp} = -0.9$ are the approximate limiting values of the anisotropy parameter for parallel and perpendicular transitions, respectively, in our apparatus^{11c-e} and β is the experimentally observed value of the anisotropy parameter. If the fast I channel results from a mixed transition to the ³Q₀ and ¹Q₁ states (ϵ_{266} for the ³Q₁ state is expected to be much smaller than that for the other states⁹), then from eq 7 we estimate that the parallel ³Q₀ state contributes 85% intensity to the electronic transition and the perpendicular ¹Q₁ state contributes 15% intensity to the electronic transition.

The high value of the anisotropy parameter ($\beta = 1.6$) for the I* channel at 266 nm indicates that I* formation arises from a prompt dissociation following a predominantly parallel electronic excitation (Figure 4b), which suggests that I* formation results from excitation to and dissociation from the alkyl iodidetype ${}^{3}Q_{0}(n,\sigma^{*})$ repulsive state as in iodobenzene.^{11a,b} However, in marked contrast to the 266 nm I* channel of iodobenzene,^{11a,b} the relative intensity of the I* channel for 3-iodopyridine at 266 nm is quite weak. The relative quantum yield of I* following the excitation of 3-iodopyridine at 266 nm is 0.022, compared to an I* relative quantum yield of 0.21 observed in iodobenzene at 266 nm.^{11a,b} This large reduction of the I* relative quantum yield in 3-iodopyridine is due to the following two facts. First, excitation to a π,π^* bound state, which yields slow I, is strongly enhanced in 3-iodopyridine. It is observed that there is a factor of ca. 4 increase in the relative quantum yield of slow I in 3-iodopyridine compared to that in iodobenzene at 266 nm. Enhanced excitation of this π,π^* bound state, which we identify as the ¹L_b band discussed later, is manifested by comparison of UV absorption spectra of the two molecules shown in Figure 2. Presumably the oscillator strength of the C-I electronic system does not change considerably in the two molecules. Second, in the prompt dissociation process due to the excitation of the ${}^{3}Q_{0}$ state of the C–I electronic system, the curve crossing probability from the ${}^{3}Q_{0}$ to the ${}^{1}Q_{1}$ state, which is responsible for the production of fast I, is largely enhanced in 3-iodopyridine

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at 266 nm. If we consider only the iodine photofragments which are produced via the prompt dissociation channel, I* and fast I, it is found that only 5% of the prompt iodine photofragments are I*, in contrast to 25% of the prompt iodine photofragments being I* in iodobenzene^{11a,b} at 266 nm. This large enhancement of the curve crossing probability is likely due to the presence of the nonbonding electrons of the nitrogen atom, which affect coupling between the ${}^{3}Q_{0}$ and the ${}^{1}Q_{1}$ state.

The results for the photodissociation of 3-iodopyridine at 266 nm suggest photodissociation mechanisms similar to those proposed for the photodissociation of iodobenzene at 266 nm.^{11a,b} An interesting difference is that the quantum yield of I produced in the slow I channel of 3-iodopyridine is greater than that observed for iodobenzene at 266 nm. Figure 1 presents the gas phase UV absorption spectrum of 3-iodopyridine. From this figure it is clear that we are exciting the ¹L_b state of 3-iodopyridine, just as it was the ${}^{1}L_{b}$ state of iodobenzene which was excited in our previous experiments at 266 nm.^{11a,b} Therefore, this observation is undoubtedly due to the fact that the molar extinction coefficient for the ${}^{1}L_{b}$ band of 3-iodopyridine ($\epsilon_{max} = 2560 \text{ L/mol} \cdot \text{cm}$) is larger (Figure 2) than that for the ¹L_b band of iodobenzene ($\epsilon_{max} = 732$ L/mol·cm). Thus, the excitation which competes with the excitation to the ${}^{3}Q_{0}$ - (n,σ^*) state is an excitation to the pyridine type $S_2(\pi,\pi^*)$ state (the ${}^{1}L_{b}$ state in Platt's notation). However, one might expect to observe a perpendicular transition for the slow I channel because of the perpendicular polarization of the pure pyridine $^{1}L_{b}$ state. The fact that a parallel transition is observed strongly suggests that, as is observed in iodobenzene,¹¹ a charge transfer (π,π^*) state, which is polarized along the C–I bond, mixes with the pyridine ${}^{1}L_{b}(\pi,\pi^{*})$ state to give the 3-iodopyridine ${}^{1}L_{b}$ state and results in the observed parallel polarization of this transition.

As with the $T_1(\pi,\pi^*)$ optical doorway state excited at 304 nm, the $S_2(\pi,\pi^*)$ state must be the optical doorway state which is predissociated by an alkyl iodide repulsive state(s) to yield the slow I photofragments. The alkyl iodide state is most likely the ${}^1Q_1(n,\sigma^*)$ rather than the ${}^3Q_1(n,\sigma^*)$ state since coupling between two states of the same spin multiplicity is more probable than coupling between states of differing multiplicities. However, mixing with the 3Q_1 state cannot be entirely dismissed because of the ability of the iodine atom to induce spin—orbit coupling. The 3Q_0 state is discounted as a predissociating state because no indirect channel is observed for the I* formation channel. A mechanism similar to that proposed for the photodissociation of 3-iodopyridine at 266 nm and written as



It is quite possible that slow I is produced via crossing from the $S_1(n, \pi^*)$ state to the ${}^1Q_1(n,\sigma^*)$ state rather than from predissociation of the $S_2(\pi,\pi^*)$ state. Internal conversion from S_2 to S_1 is known to be rapid²⁷⁻³⁵ and becomes more rapid as the S_2-S_1 energy gap is decreased. The presence of the iodine atom certainly red-shifts the $S_2(\pi,\pi^*)$ state and blue-shifts the $S_1(n,\pi^*)$ state and thus narrows the energy gap. Thus it is possible that, following excitation to S_2 , rapid internal conversion to S_1 occurs, followed by crossing to 1Q_1 or 3Q_1 . Thus a modified mechanism for the photodissociation of 3-iodopyridine to produce slow I at 266 nm can be written as

$${}^{1}A_{1} \xrightarrow{h_{V}} S_{2}(\pi, \pi^{*})$$

$$\begin{cases} fast \\ internal \\ conversion \\ S_{1}(n, \pi^{*}) \xrightarrow{1 \text{ or } 3(n, \sigma^{*})} \xrightarrow{} I(slow) \end{cases}$$

C. The Dependence of Internal Energy Redistribution of the Prompt I and I* Channels on Excess Energy. We observe a strong photon energy dependence of the internal energy of the pyridine radical for the fast I and I* photodissociation channels at 266 nm (Figure 9), which, as in the photodissociation of iodobenzene¹¹ and CF₃I,^{8c,24} indicates that pyridine ring vibrational modes are strongly coupled to the dissociation along the carbon-iodine dissociation coordinate in the fast I and I* channels. This strong coupling undoubtedly results in energy transfer from the optical doorway state to the dark states. This rate of energy transfer, which is the transition rate $w_{i\rightarrow [n]}$ between the optical doorway n, σ^* state (represented by the letter i) and the dark vibronic π,π^* and n, π^* states (represented by [n]), is given by Fermi's Golden Rule:

$$w_{i \to [n]} = (2\pi/\hbar) \varrho(E_n) |\langle \psi_n | V | \psi_i \rangle|^2$$
(8)

where $\rho(E_n)$ is the density of the π,π^* and n,π^* vibronic states at the n,σ^* excitation energy, and $\langle \psi_n | V | \psi_i \rangle$ is the electronic matrix element coupling the n,σ^* optical doorway state with the various π,π^* and n,π^* dark states. In comparison to iodobenzene, 3-iodopyridine certainly has a larger density of states due to the nonbonding pair of electrons, and thus it is reasonable to expect energy transfer to be more rapid in 3-iodopyridine than in iodobenzene.

The fully widths at half-maximum (fwhm's) of the translational energy distributions for the fast I and I* channels are manifestations of the rates of internal energy redistribution described by the Golden Rule. Equations 5 and 6 state that during photodissociation energy will be deposited into the internal energy modes of the polyatomic photofragment, which implies that the translational energy distribution will have a width which reflects the excitation of rovibronic states. For the photodissociation of iodobenzene,^{11b} we proposed that the rate of energy redistribution, which is in direct competition with prompt dissociation from *the same electronic state*, increases with the density of the nearby phenyl π, π^* dark states.

Figure 10 presents a comparison of the dependence of the fwhm on $\langle E_{avl} \rangle$ for the fast I and I* channels of 3-iodopyridine and iodobenzene. It is clear that the fwhm's for both the fast I and I* channels increase more with $\langle E_{avl} \rangle$ for 3-iodopyridine than for iodobenzene. That is, the rate of energy redistribution increases more rapidly with the excitation photon energy for 3-iodopyridine than for iodobenzene. This is consistent with the Golden Rule and correlates with the likely fact that the density of vibronic states in 3-iodopyridine increases faster than does the density of vibronic states in iodobenzene.

D. The Time Dependence of the Translational Energy Release and the Rates of Internal Energy Redistribution (IER) in the Slow I Channel. The lifetime of the transition state is actually represented by a range of lifetimes, not just a single lifetime. This is because the redistribution of the excess available energy, $\langle E_{avl} \rangle$, into the internal energy modes is quite efficient and could compete effectively with the carbon-iodine bond dissociation. That is, predissociation from the bound state competes with nonradiative processes which must be occurring on the subpicosecond timescale.^{11c-e} If we assume that the dependence of β on E_T is a result of molecular rotation occurring on the dissociation time scale, we can determine the dependence of E_T on the dissociation time t (Figure 8). The time dependences of the translational energy release are roughly linear in the range of the low translational energy distributions observed at 304 nm and 266 nm, which is what is observed in iodobenzene.¹¹ The negative of the slope of the time dependence of the translational energy release, $-dE_T/dt$, has been shown to be simply the rate of internal energy redistribution (IER),^{11c-e} following photoexcitation of the π,π^* optical doorway state.

At 304 nm, the rate of IER is found to be about 22 kcal/ mol·ps, which is comparable to that observed for iodobenzene at 304 nm (23 kcal/mol·ps).^{11c-e} It is surprising that the rate of IER observed at 304 nm in 3-iodopyridine is not larger than that observed in iodobenzene at 304 nm¹¹ since the availability of the triplet n, π^* levels might be expected to provide for more efficient internal conversion.²⁷⁻³⁵ It is known^{30,31} that the rate of internal conversion between π,π^* and n,π^* states depends on the energy gap between these states; as the energy gap decreases, the rate of internal conversion increases. Recall that in pyridine the ${}^{3}A_{1}(\pi,\pi^{*})$ and ${}^{3}B_{1}(n,\pi^{*})$ states are nearly degenerate. It is not known what the energies of the 3-iodopyridine triplet states are. However, it is likely that the ${}^{3}(\pi,\pi^{*})$ state will shift to a lower energy and the $^{3}(n,\pi^{*})$ state will shift to a higher energy, thus breaking the degeneracy. This assumption is based on studies²⁰ in which singlet n, π^* and π, π^* states were found to blue-shift and red-shift, respectively, upon halogenation. Breaking the degeneracy of the ${}^{3}A_{1}$ and ${}^{3}B_{1}$ states will certainly reduce the efficiency of internal conversion between these states. Therefore, unlike the 266 nm region, the densities of states of 3-iodopyridine and iodobenzene in the 304 nm region become comparable, resulting in comparable rates of IER in 3-iodopyridine and iodobenzene at 304 nm.

At 266 nm the rate of IER dramatically increases to about 39 kcal/mol-ps, in contrast to iodobenzene, in which the rate of IER decreases to 15 kcal/mol-ps at 266 nm from 23 kcal/ mol-ps at 304 nm.¹¹ One reason is undoubtedly the higher density of vibronic states available for excess energy disposal as compared to iodobenzene. In iodobenzene in the 266 nm region there are the $S_1(\pi,\pi^*)$ and $T_2(\pi,\pi^*)$ states available for IER.¹⁴⁻¹⁶ In 3-iodopyridine, the states available for IER are the S₂(π,π^*) state and the closely spaced T₃(π,π^*) and T₄(π,π^*) states. Furthermore, there is the $S_1(n,\pi^*)$ state energetically below the $S_2(\pi,\pi^*)$ state. As stated previously, it is well known that, in general, $\pi, \pi^* \leftrightarrow n, \pi^*$ internal conversion is extremely efficient in the nitrogen heterocycles.²⁷⁻³⁵ The energy gap between the S₁(n, π^*) state and the S₂(π,π^*) state in pyridine is relatively small (\sim 3500 cm⁻¹),³⁵ and it is reasonable to assume that substitution of iodine red-shifts the $S_2(\pi,\pi^*)$ state and blueshifts the $S_1(n,\pi^*)$ state,²⁰ thus causing the energy splitting between these two states to be even smaller, possibly negligible, in 3-iodopyridine. This compression of vibronic levels certainly enhances the already efficient vibronic coupling between the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ states and is thus likely responsible for the larger rate of IER observed at 266 nm.

E. Quantum Yields for Dissociative and Radiationless Transitions at 266 nm for the Slow I Channel.³⁶ For each of the excitation/photodissociation mechanisms proposed for 3-iodopyridine, it is reasonable to assume that following excitation to the repulsive state the overall quantum yield of the fast I and I* photoproducts will be unity. On the other hand, it is also reasonable to assume that the quantum yield of slow

I photofragments from the predissociative pyridine π,π^* optical doorway bound states is less than unity. That is, a fraction of the molecules excited to the ${}^1L_b(\pi,\pi^*)$ state will dissociate, and the remaining will undergo internal energy redistribution via different competing radiative and nonradiative pathways. Therefore, in order to determine the quantum yields of fast I, I*, and slow I, we consider the transition to the repulsive state and the transition to the predissociated bound state separately. The quantum yields for fast I and I* formation, $\Phi(I_{fast})$ and $\Phi(I^*)$, respectively, are given by

$$\Phi(\mathbf{I}_{\text{fast}}) = \frac{n(\mathbf{I}_{\text{fast}})}{n(\mathbf{I}_{\text{fast}}) + n(\mathbf{I}^*)}$$
(9a)

and

$$\Phi(\mathbf{I}^*) = 1 - \Phi(\mathbf{I}_{\text{fast}}) \tag{9b}$$

where $n(I_{fast})$ and $n(I^*)$ are the numbers of fast I and I*, respectively, produced via the prompt alkyl iodide-type dissociation process only. From this treatment we find that for the prompt alkyl iodide-type dissociation in 3-iodopyridine $\Phi(I_{fast}) = 0.95$ and $\Phi(I^*) = 0.05$ at 266 nm.

We now consider the quantum yield of slow I, $\Phi(I_{slow})$, and the quantum yield of molecules, Φ_{NR} , which do not dissociate following excitation to the ${}^{1}L_{b}(\pi,\pi^{*})$ bound state at 266 nm. From our knowledge of the relative yields of I*, fast I, and slow I (see Table 1), and from our knowledge of the molar extinction coefficients of 3-iodopyridine ($\epsilon_{266} = 2560$ L/molcm) and methyl iodide^{11a} ($\epsilon_{266} = 270$ L/mol-cm), we are able to estimate the quantum yields of both the slow I photofragments and the molecules which do not dissociate following photoexcitation to the ${}^{1}L_{b}$ doorway state at 266 nm. We have determined the relative yields of slow I to be $F(I_{slow}) = 0.56$ for 3-iodopyridine. Since we consider the alkyl iodide, n,σ^* and aromatic π,π^* electronic transitions to be essentially localized, 10a, 12, 13 the absorption intensities of the respective ${}^{1}L_{b}$ bands observed in the UV spectra of iodobenzene and 3-iodopyridine simply result from the superposition of the alkyl iodide and aromatic electronic absorption intensities. From this discussion we find that for the localized transition to the ${}^{1}L_{b}$ state of 3-iodopyridine $\epsilon_{266} = 2290$ L/mol-cm. These values for the extinction coefficients at 266 nm are actually larger than those for the absorption maxima of the ${}^{1}L_{b}$ bands of pyridine (2000 L/mol-cm).³⁷ This can be explained by the fact that the transition to the ${}^{1}L_{b}$ state is a symmetry forbidden transition which is weakest in benzene because of that molecule's high symmetry, but becomes stronger as the symmetry is lowered. Thus the substitution of an iodine atom onto benzene and pyridine lowers the symmetry of these molecules and should therefore enhance the intensity of the transition to the ${}^{1}L_{b}$ state. It can be shown that

and

where

$$\Phi_{\rm NR} = 1 - \Phi(I_{\rm slow}) \tag{10b}$$

(10a)

 $X_{\rm max} = \epsilon_{266}(A) / \epsilon_{266}(CH_3 I) = 8.5$ (11)

where A = pyridine, $F(I_{slow})$ is the relative yield of slow I (0.56), $F(I_{fast})$ is the relative yield of fast I (0.42), and $F(I^*)$ is the relative yield of I* (0.02). From this method of analysis we find that for 3-iodopyridine $\Phi(I_{slow}) = 0.15$ and $\Phi_{NR} = 0.85$.

 $\Phi(\mathbf{I}_{slow}) = F(\mathbf{I}_{slow}) / [F(\mathbf{I}_{fast}) + F(\mathbf{I}^*)] X_{max}$

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In this treatment, we have assumed that all of the excited molecules which do not dissociate decay nonradiatively; in fact, there are radiative decay pathways. However, since the quantum yields of fluorescence and phosphorescence are known to be much smaller than the quantum yields of nonradiative decay processes (internal conversion, intersystem crossing, intramolecular vibrational relaxation) in pyridine,^{30,31} we expect this to be the case in 3-iodopyridine as well. Therefore, our nonradiative quantum yields should closely approximate the true nonradiative quantum yields.

F. Kinetics Considerations: The Nonradiative Relaxation Processes Observed in the Slow I Channel of 3-Iodopyridine at 266 nm. Upon photoexcitation of the ${}^{1}L_{b}$ doorway state, dissociation competes with the redistribution of internal energy. Within a given translational energy release window ΔE_{T} , a fraction of the excited molecules, $\Phi(I_{slow})$, will dissociate to give slow iodine photofragments, while the rest of the excited molecules, Φ_{NR} , will not dissociate. Because we are able to estimate the quantum yield of 3-iodopyridine molecules which do not dissociate following excitation to the ${}^{1}L_{b}$ state, we are able to use this information in conjunction with the rates of IER to estimate rate constants for nonradiative decay processes which compete with predissociation.

In order to estimate the nonradiative rate constant, $k_{\rm NR}$, it is necessary to determine the nonradiative decay time $\tau_{\rm NR}$. From Figure 6b we find that for the low $E_{\rm T}$ distribution $G_1(E_{\rm T})$ the translational energy range $\Delta E_{\rm T}$ is about 26 kcal/mol, which is also the internal energy distribution. Therefore, the time it takes to produce the slow I photofragments observed within the resolution of our experiment (i.e., the time dependence of G_1 - $(E_{\rm T})$) is the nonradiative decay time $\tau_{\rm NR}$. From $\Delta E_{\rm T}$ and the rate of IER, $-dE_{\rm T}/dt$, $\tau_{\rm NR}$ is given by

$$\tau_{\rm NR} \simeq \Delta E_{\rm T} / (-dE_{\rm T}/dt) \tag{12}$$

For 3-iodopyridine ($\Delta E_{\rm T} = 26$ kcal/mol, $-dE_{\rm T}/dt = 39$ kcal/ mol-ps), we calculate the average nonradiative decay time following photoexcitation of the $S_2(\pi,\pi^*)$ state at 266 nm to be $\tau_{\rm NR} = 0.67$ ps.

The rate constants for the competing dissociation and nonradiative decay processes are given by

$$k(\mathbf{I}_{slow}) = \Phi(\mathbf{I}_{slow})/\tau_{NR}$$
(13)

and

$$k_{\rm NR} = \frac{1 - \Phi(I_{\rm slow})}{\tau_{\rm NR}} = \frac{\Phi_{\rm NR}}{\tau_{\rm NR}}$$
(14)

where $k(I_{slow})$ and k_{NR} are the rate constants for the formation of slow I and the nonradiative decay of the excited molecules, respectively. Because of the extremely large density of states which results from the presence of the alkyl iodide repulsive continuum, we treat 3-iodopyridine in the statistical-limit case.^{30,33} From this analysis we estimate the rate constants for relaxation and for slow I dissociation for 3-iodopyridine at 266 nm to be $k_{NR} = 1.3 \times 10^{12} \text{ s}^{-1}$ and $k(I_{slow}) = 2.2 \times 10^{11} \text{ s}^{-1}$.

The nonradiative rate constant, which represents internal energy redistribution into the various pyridine vibronic modes, determined for the slow I photodissociation channel of 3-iodopyridine at 266 nm is comparable to, if not actually larger than, the observed rate of 10^{12} s^{-1} for nonradiative decay in pyridine³⁰ at an excess energy of 700 cm⁻¹ in the S₂(π,π^*) state.³⁸ It has been proposed that this rate constant in pyridine corresponds to the rate of S₁ \rightarrow S₀ internal conversion. An increase in the rate of nonradiative decay would be consistent with theoretical predictions²⁹ and experimental observations^{30,31} that the rate of radiationless transitions increases as the $S_2(\pi,\pi^*)-S_1(n,\pi^*)$ energy gap decreases. In the azabenzenes, n,π^* and π,π^* states are well known²⁹ to strongly couple vibronically. Lowering the energy gap between n,π^* and π,π^* states allows the lower frequency out-of-plane vibrations to become more active in vibronic coupling,²⁹ with the consequence being that the rate of $S_1 \rightarrow S_0$ internal conversion increases. Substitution of an iodine atom onto the pyridine ring will certainly red-shift the $S_2(\pi,\pi^*)$ state and may slightly blue-shift the $S_1(n,\pi^*)$ state, resulting in a reduction of the pyridine S_2-S_1 energy gap³⁰ from about 3600 cm⁻¹ to about 2200 cm⁻¹. However, we do not observe any dramatic increase in the nonradiative decay rate upon substitution of an iodine atom. This is because $k_{\rm NR}$ represents energy redistribution into pyridine modes other than C-I modes. Energy redistribution into C-I modes results in predissociation, which we monitor by detecting slow I photofragments. Thus the rate of energy redistribution into the C-I modes is given by $k(I_{slow})$. The presence of the C-I n, σ^* dissociative continuum appears to have little effect on the nonradiative processes governing energy redistribution into the pyridine modes. It is therefore likely that the $S_2(\pi,\pi^*) \rightarrow$ $S_1(n,\pi^*) \rightarrow S_0$ internal conversion sequence likely remains the dominant nonradiative mechanism for internal energy redistribution in 3-iodopyridine.

Another nonradiative process which might also be enhanced upon the substitution of an iodine atom onto the pyridine ring is intersystem crossing (ISC). Intersystem crossing is well known to occur efficiently in the azabenzenes²⁹⁻³² owing to the strong spin-orbit coupling observed in these molecules. Addition of an iodine atom will undoubtedly enhance the spinorbit coupling and increase rates of intersystem crossing. However, because luminescence is not measured in our experiment, we are unable to differentiate between intersystem crossing and internal conversion (IC) in 3-iodopyridine. Rate constants of ISC in azabenzenes³⁰ are, however, typically on the order of $10^9 - 10^{10} \text{ s}^{-1}$, i.e., at least two orders of magnitude less than the rate constants for internal conversion. Nonetheless, we can only say that the nonradiative rate constant $k_{\rm NR}$ obtained above is a rate constant which includes all of the possible nonradiative decay processes which do not lead to the formation of iodine photoproducts.

Conclusions

For the photodissociation of 3-iodopyridine at 304 nm and 266 nm we observe multiple dynamical processes occurring at each wavelength in the ground state I channel and a single process in the I* channel. At 304 nm, it is proposed that the fast I and I* channels result from excitation to the alkyl iodide ${}^{3}Q_{0}(n,\sigma^{*})$ state, followed by crossing to the ${}^{1}Q_{1}(n,\sigma^{*})$ state for fast I, while the slow I channel is proposed to result from excitation to the 3-iodopyridine $T_{1}(\pi,\pi^{*})$ optical doorway bound state which is predissociated by mixing with the an alkyl iodide n,σ^{*} repulsive state(s). At 266 nm, the proposed mechanism involves excitations to the 3-iodopyridine ${}^{1}L_{b}(\pi,\pi^{*})$ optical doorway state, which is predissociated by mixing with the alkyl iodide ${}^{1}Q_{1}(n,\sigma^{*})$ dissociative state to yield slow I, and to the alkyl iodide ${}^{3}Q_{0}(n,\sigma^{*})$ repulsive state, which yields I* directly and fast I by crossing to the ${}^{1}Q_{1}(n,\sigma^{*})$ state.

As we proposed for the fast I and I* channels of iodobenzene,¹¹ in analogy with CF_3I ,^{8c},²⁴ the observed strong photon energy dependence of the internal energy of the aromatic ring indicates a strong coupling of the pyridine ring vibrational modes to the carbon–iodine dissociation coordinate. The strong photon energy dependences of the fwhm's of the fast I and I* translational energy distributions indicate that the rate of energy redistribution which competes with the prompt dissociation processes correlates with the amount of excess energy, due to the increasing density of vibronic dark states of the aromatic ring.

The observed increase in the rate of IER from 22 kcal/molps at 304 nm to 39 kcal/mol-ps in the slow I channel at 266 nm implies the increased density of states at 266 nm compared to that at 304 nm due to a closer isoergicity of $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ vibronic levels. While the rate of IER at 304 nm is comparable to the rate of IER in iodobenzene at 304 nm,^{11c-e} the rate of IER observed at 266 nm for 3-iodopyridine is significantly larger than the rate of IER observed in iodobenzene^{11a,b} at 266 nm. The observations are consistent with the fact that while the density of states in 3-iodopyridine in the 304 nm region is comparable to the density of states in iodobenzene in the same energy region, at 266 nm the density of states of 3-iodopyridine is significantly larger than in iodobenzene. Our estimated value for the observed nonradiative rate constant $k_{\rm NR}$ at 266 nm for 3-iodopyridine is comparable to the value of $k_{\rm NR}$ measured by luminescence studies on pyridine³⁰ at a similar excess energy, indicating the mixing of the pyridine-type bound states with the alkyl iodide-type n,σ^* dissociative continuum is the dominant factor which determines the excited state lifetime.

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