progress of the reaction. Once the gas evolution ceased, the mixture was subjected to vacuum distillation to afford 16.9 g (89.9%) of 2-n-butyl-5,6-dihydro-4H-1,3-oxazine as a colorless oil: bp 62-64 °C(12 mmHg); TLC R_f 0.69 (MeOH/CHCl$_3$, 1/9); ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.20 (t, 2H,-OC$\underline{H}_3$-), 3.21 (t, 2H, =NC$\underline{H}_2$-), 2.05 (t, 2H, -C$\underline{H}_2$CH$_2$CH$_2$CH$_3$-), 1.75 (m, 2H, -CH$_2$C$\underline{H}_2$CH$_2$-), 1.40 (m, 4H, -CH$_2$C$\underline{H}_2$C$\underline{H}_2$CH$_3$-), 0.85 (t, 3H, -C$\underline{H}_3$); IR (neat) 1670 (-C=N-), 1080 (-C-O-C-) cm^{-1}; EI-MS m/z (relative intensity) 140 (1.40), 126 (11.25), 112 (24, 76), 99 (100.00), 84 (12.98), 71 (17.86), 57 (14.17), 41 (21. 23).

Based upon our observations during the reaction, we proposed the following reaction mechanism (Scheme 1).

The nitrile was activated by the coordination of Lewis acid catalyst (ZnCl$_2$, Zn(OAc)$_2$, Cu(OAc)$_2$) and attacked by 3-amino-1-propanol **1** to form the key intermediate **7**. Following prototropic rearrangement and cyclization afford 5,6-dihydro-4H-1,3-oxazine **12** with the expulsion of ammonia irreversibly driving the reaction to completion. All of nitriles and aminoalcohols that we tried afforded moderate to good yields. The yield of the reaction was increased as the carbon of alkyl group in nitrile increased because of the stability of these products at the stage of distillation. Zinc chloride showed better catalytic reactivity than zinc acetate or copper acetate.

In conclusion, a facile synthetic route for various 1,3-oxazine derivatives has been developed. Application of these compounds to the ring opening polymerization is currently under investigation in our laboratory.

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11. All compounds were fully characterized by spectroscopic methods. All yields refer to be isolated compounds.

The v-J Correlation in the photodissociation of t-butyl hydroperoxide at 266 nm

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A detailed study on photodissociation dynamics of polyatomic molecules requires precise measurements of certain experimental observables. Among these experimental observables, internal and translational energy distribution among fragments are scalar properties while angular distribution of the fragments, transition dipole moment, and rotational angular momenta are vector properties. In order to study the dynamics and mechanism of the process in detail, correlations between these vector properties are especially important. Experimentally, if the photofragments absorb or emit radiation of easily accesible spectral region, Doppler profiles of the spectra can provide such valuable information on the photodissociation process.[1~3]

When the photofragments are polyatomic molecules, the fragments have rotational angular momenta J which have definite relationship with the recoil velocities. Since this v-J correlation is developed when the fragmentation occurs, the v-J correlation may appear even when the angular distribution is isotropic. For example, let's consider J is predominantly aligned parallel to the recoil direction (out-of-plane dissociation). When the Q-branch transition is probed where transition dipole moment of the fragments μ_a is parallel to J in the classical limit, the fragments moving in the direction of propagation of the probe light k_p, will absorb photons at the wings of the Doppler profiles. On the other hand, the fragments moving in the plane perpendicular to k_p will absorb at the center of the profiles. Since the absorption takes place when μ_a is parallel to $\varepsilon_p(\perp k_p \| z)$, the profile shows a maximum at the center. Contrary to the Q-branch transitions, when the P and R-branch transitions are probed where μ_a is perpendicular to J, the Doppler profiles show the minimum at the center. In this case, the observed Doppler profiles are given by

$$I(v)=(4\pi)^{-1}[1+\beta_{eff}P_2(\cos\ \theta_{v,z})P_2(\cos\ \theta_{\varepsilon,z})]$$

where P_2 is the second order Legendre Polynomials and β_{eff} includes all the vector correlations. $\theta_{v,z}$ and $\theta_{\varepsilon,z}$ are angles between the propagation direction of the probe light and the recoil velocity, the electric vector of the dissociating light, respectively.

t-Butyl hydroperoxide is one of the good candidates to study detailed photodissociation dynamics using the Doppler spectroscopy because most of the available energy is known to be transformed into product translation at 248 nm.[4] The large translational energy of the fragments can provide the Doppler shift wide enough to be measured with conventional laser spectroscopic techniques such as laser induced fluorescence (LIF).

The LIF spectra of the fragment OH have been measured in a flow cell with a conventional pump-probe geometry. The
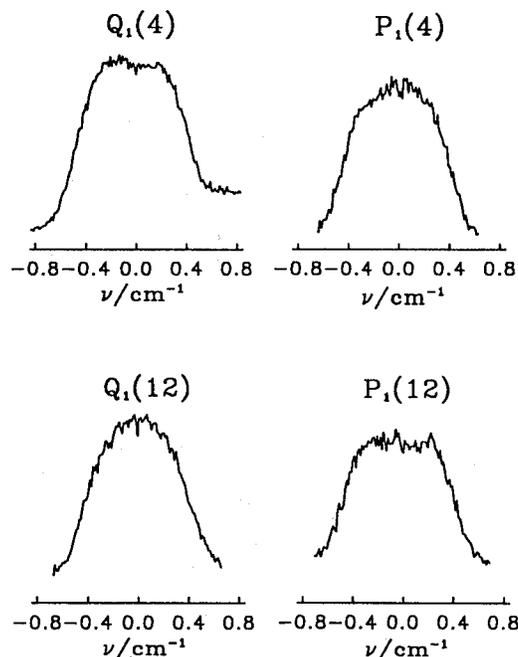
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Figure 1. Measured Doppler profiles for the P_1 and Q_1 rotational transitions at N=4 and N=12 under the $\varepsilon \perp z$ experimental geometry. The band origins are given in the literature (Ref. 5).

cell has been evacuated and about 30 mTorr of the gaseous sample has been flowed through the cell. The dissociating light is the 4th harmonic of an Nd : YAG laser (Lumonics YM800), which is horizontally polarized. The probe light is obtained from a tunable dye laser (Lumonics HD500) pumped by the 2nd harmonic of the same Nd : YAG laser which is delayed by about 10 ns. The dye laser output is frequency doubled through a KDP crystal to probe OH employing the 0-0 band of the A←X electronic transition in UV. The two laser beams are collinearly counterpropagated through the cell or crossed at a right angle at the center of the cell. These two experimental geometries provide $\varepsilon \perp z$ for the former and $\varepsilon \| z$ for the latter. The induced fluorescence is focused onto a PMT (Hamammatsu R211UH) equipped on top of the plane formed by the two laser beams. The detected signal is fed to a boxcar with a signal processor and the digitized signal is stored in a PC.

The LIF spectra of OH for the $P_1(4)$, $Q_1(4)$, $P_1(12)$, and $Q_1(12)$ transitions under the experimental geometry $\varepsilon \perp z$ are presented in Figure 1. The spectral assignments are given by Dieke and Crosswhite.[5] The spectra for the same transitions have been measured for the other experimental geometry but no significant differences have been observed. The Doppler profiles can be described by an expansion into bipolar spherical harmonics ignoring the higher order terms, and the profiles are given by[6,7]

$$I(v) \propto g_0/2\Delta v_D[1+g_2/g_0P_2(\cos \theta_{v,z})]$$

where Δv_D is the maximum Doppler shift and the g's are

$$g_0 = b_0 + b_1\beta_0^2(02)$$

$$g_2 = b_2\beta_0^2(20) + b_3\beta_0^0(22) + b_4\beta_0^2(22).$$

The bipolar moments $\beta_0^2(02)$ represents the rotational align-

ment (μ-J correlation), $\beta_0^2(20)$, the translational anisotropy, $\beta_0^0(22)$, the υ-J correlation, and $\beta_0^2(22)$, the μ-υ-J correlation, respectively. The multipliers, b's, defined by Dixon,[6] are obtained from the experimental geometries and different rotational branches. Compared to the experimental Doppler profiles, β_{eff} is obtained as

$$\beta_{eff} = \frac{g_2}{g_0P_2(\cos \theta_{\varepsilon,z})}.$$

Since the observed profiles show no significant differences between the two experimental geometries, the angular distribution of the recoil velocities must be isotropic, and therefore the rotational anisotropy, the μ-J correlation can also be ignored. Thus, β_{eff} under our perpendicular $\varepsilon \perp z$ geometry is approximated to be

$$\beta_{eff} = -\frac{2b_3\beta_0^0(22) + 2b_4\beta_0^2(22)}{b_0}$$

The measured Doppler profiles for different rotational branch transitions from the same rotational state N are fitted with β_{eff} and then $\beta_0^0(22)$ and $\beta_0^2(22)$ are obtained from β_{eff} and b's by Dixon.

The measured υ-J correlations, $\beta_0^0(22)$'s are -0.4 ± 0.2 at N=4 and 0.3 ± 0.1 at N=12. As is mentiond above, the positive υ-J correlation implies the out-of-plane dissociation as represented by $\upsilon \| J$ while the negative υ-J correlation implies in-plane-dissociation, $\upsilon \perp J$. The rotational motion of the OH fragments may originate from the impulse upon dissociation, which is estimated much lower by an impulsive model.[8] Concerning vibrational motions in the parent molecule whose energy can in part be transformed into the product rotation, the available motions are in-plane bending and torsional motion of the OH moiety. The in-plane bending motion can give $\upsilon \perp J$ and the negative υ-J correlation when the structure of the parent molecule remains trans planar upon excitation while the torsional motion should give $\upsilon \| J$ and the positive υ-J correlation. The measured υ-J correlation suggests that the torsional motion of the parent t-butyl hydroperoxide molecule plays more important role to the rotation of the OH fragments at higher N. The complete vector correlations and energy distributions have been being measured in our laboratory and will be published in the future.

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