For the reactions with carboxylic esters, the anion **4** was prepared, the solvent was removed under vacuum, cyclohexane and the ester were added, and the mixture was refluxed overnight and worked up with aqueous acid.

Deprotonation of boronic esters may have wide-ranging synthetic utility, inasmuch as other types of substituted boronic esters can also be deprotonated to boron substituted carbanions.[8,9]

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Received January 28, 1977

Laser Induced Isotope Enrichment in a Rare Gas Matrix

Sir:

Since the initial report by King and Hochstrasser[1] on the first successful low temperature laser induced isotope separation in mixed molecular crystals of *s*-tetrazine, considerable attention has been given to this technique as well as to the photochemistry and spectroscopy of this interesting chromophore.[2-5] For example, King, Denny, Hochstrasser, and Smith[4] recently demonstrated that 1,4-nitrogen bonding plays a negligible role in the overall photochemical decomposition leading to nitrogen and HCN. Furthermore, it was noted that low temperature high resolution mixed crystal spectroscopy was a novel method for the nondestructive analysis of isotopic composition as well as a useful tool for the determination, at natural abundance, of spectroscopic parameters of rare isotopically substituted species.

The scope of solid state isotope separation and analysis, however, has been severely limited by the general requirement for high quality mixed crystals. It is a difficult problem to find a suitable host species for each new chromophore. With this consideration in mind we report here on high resolution optical spectroscopy of a photochemically unstable species in a rare gas matrix at low temperature. In addition, the results of laser induced isotope enrichments and photochemical studies are presented. The system chosen for study was *s*-tetrazine in argon.

Matrices of *s*-tetrazine[6] in argon were deposited on a polished LiF window, maintained at 10 K, via three techniques: slow uniform deposition at a rate of ca. 0.5 L Torr h^{-1}, rapid deposition at 5-10 L Torr h^{-1}, and pulsed deposition in 10 μmol aliquots. Typical argon:tetrazine mole ratios (M/R) were ca. 1000. Examination of the $^1B_{3u} \leftarrow {}^1A_g$ ($n\ \pi^*$) band region of a fresh *s*-tetrazine-argon matrix at moderate resolution revealed the presence of several sites. However, approximately 90% of the observed spectral intensity was due to *s*-tetrazine chromophores with their origin band at 17 926 cm^{-1}. The bandwidths of these unannealed spectra were 3-5 cm^{-1} regardless of the method used for the deposition. Annealing to 40 K produced two dramatic changes. First, there was a considerable decrease in the observed vibronic transition line widths to ca. 0.5 cm^{-1}. Second, an additional set of absorption bands which were reduced in intensity in matrices of M/R ~ 2000, appear to higher energy than the O-O and vibronic bands in matrices of M/R = 1000. These new bands result from aggregation.

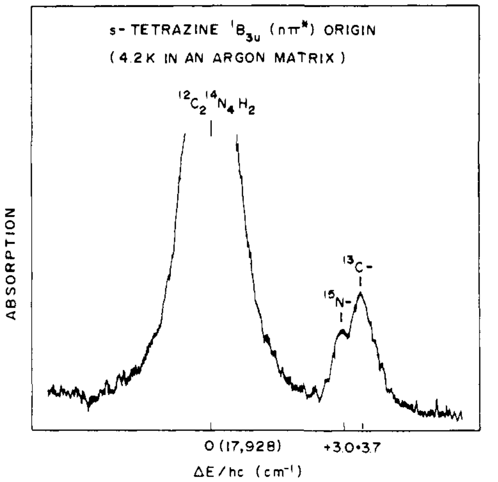

Figure 1. The absorption of the *s*-tetrazine $^1B_{3u} \leftarrow {}^1A_g$ O–O band in an argon matrix at 4.2 K. The spectrum was photographed on a 2-m Jarrell-Ash spectrometer in 15th order. A 450-W Xe lamp was used as the background continuum.

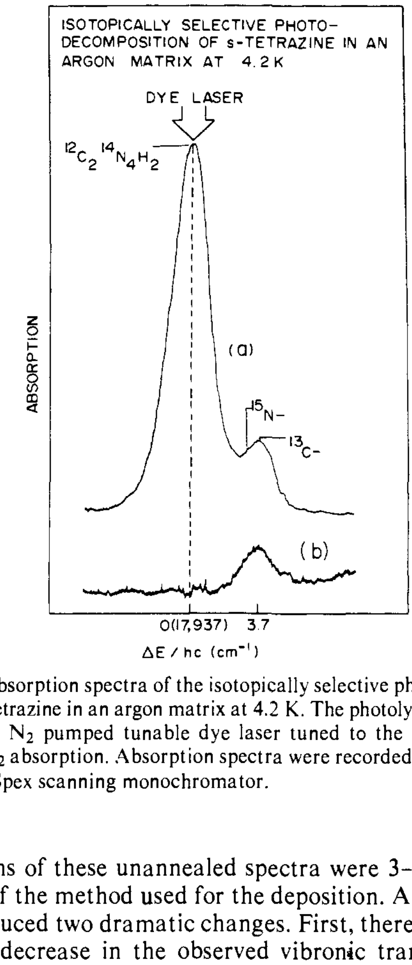

Figure 2. Absorption spectra of the isotopically selective photodecomposition of *s*-tetrazine in an argon matrix at 4.2 K. The photolysis source was a 0.6 cm^{-1} N_2 pumped tunable dye laser tuned to the region of the $^{12}C_2{}^{14}N_4H_2$ absorption. Absorption spectra were recorded photoelectrically on a Spex scanning monochromator.

The strongest O-O band site of annealed *s*-tetrazine in argon (M/R = 1000) at 4.2 K was measured at 17 928.4 cm^{-1} (cf. Figure 1). Two sharp spectral features associated with this peak at 17 931.4 and 17 932.1 cm^{-1} were observed with relative intensities of 0.71:1. These are the O-O transitions of *s*-tetrazine-$^{15}N_1$ and *s*-tetrazine-$^{13}C_1$ in argon, respectively.

Assignments were made by comparisons with the zero-point isotopic shifts observed for naturally abundant *s*-tetrazine in mixed molecular crystals[2] at 1.6 K and by their observed relative intensities in absorption (i.e., expect a ratio of 0.64:1.0 from natural abundances).

The Franck-Condon maximum of the $^1B_{3u} \leftarrow {}^1A_g$ transition is at the $6a_0{}^1$ band. Unlike the O-O band region, the rare (heavier) isotopic species absorb at lower energies than the more abundant species in the vibronic bands. The overall separations of the $6a_0{}^1$ transitions of *s*-tetrazine-$^{15}N_1$ and *s*-tetrazine-$^{13}C_1$ from that of *s*-tetrazine in argon at 4.2 K are 5.9 and 12.2 cm^{-1}, respectively. Dye laser excitation (spectral bandwidth 0.6 cm^{-1}) of a single isotopic species resulted in fluorescence exclusively from the particular single isotope originally excited.

The spectra of *s*-tetrazine in an argon matrix were bleachable by a few minutes of dye laser irradiation. Low temperature infrared experiments on photolyzed matrices demonstrated that the only infrared active photoproduct was HCN. Interestingly, the HCN was present exclusively as HCN dimers. This result indicates that there was very likely considerable motion of the HCN subsequent to its photochemical generation, as the stable dimer structure of HCN is known to involve head-to-tail hydrogen bonding (i.e., HCN···HCN).[7]

Finally, the results of the laser induced isotopic segregation are shown in Figure 2. Here, the origin region of *s*-tetrazine in argon at 4.2 K (M/R = 1000) is shown in absorption at moderate resolution (ca. 0.8 cm^{-1}). The matrix sample containing 0.5 mg of *s*-tetrazine was irradiated at 17 928 cm^{-1} ($C_2N_4H_2$) with a 0.6 cm^{-1} bandwidth dye laser (10 kW peak power, 50 Hz, 6 ns) for 5 min. The sample was probed in absorption for isotopic composition. Figure 2a represents a moderate resolution absorption spectrum of a virgin sample (i.e., natural abundances of nitrogen-15 and carbon-13) while Figure 2b demonstrates the isotopically selective photochemical removal of *s*-tetrazine ($C_2N_4H_2$) thereby generating pure HCN and N_2. Identical procedures may be used to selectively photolyze *s*-tetrazine-$^{15}N_1$, *s*-tetrazine-$^{13}C_1$, or even less abundant isotopic species such as *s*-tetrazine-$^2H_1$.

The principal result of this work is the demonstration that a photochemically unstable system can be deposited in an argon matrix with sufficient homogeneity that naturally abundant isotopic molecules can be clearly distinguished. The observed line widths of ca. 0.7 cm^{-1} were sufficiently narrow that a tunable laser could be used to selectively decompose different isotopic species. This result has preparative implications since both the photolysis products (HCN and N_2) and the inert lattice can be completely removed and purified from the unphotolyzed tetrazine.

A literature survey of optical spectra obtained from matrix isolated species reveals that the spectral line widths achieved here are not common. We, however, have found in a number of systems that when the deposition and annealing procedures and the vapor phase composition are systematically optimized, the spectral line widths obtained are a few tenths of cm^{-1} and are therefore perfectly suitable for isotopically selective chemistry. The technique of matrix isolation combined with tunable laser excitation offers a substantial practical advance over previous mixed crystal methods, since the search for appropriate organic host lattices is circumvented.

Additional examples of laser induced isotope separation at low temperature in rare gas matrices will be discussed in later reports.

Acknowledgments: It is a pleasure to acknowledge the partial support of this investigation by the National Science Foundation (No. CHE 75-16177) and the Material Research Laboratory at the University of Pennsylvania (No. DMR 76-00678).

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Received February 7, 1977

Generation of Peroxy Radicals from Peroxy Nitrates (RO_2NO_2). Decomposition of Peroxyacyl Nitrates

Sir:

The study of the chemistry of peroxy radicals has been largely limited to indirect sources such as autooxidation of hydrocarbons and generation of nonoxygenated radicals by photolysis in the presence of oxygen.[1,2] To develop a source of acylperoxy radicals suitable for studying reactions under atmospheric conditions, we have investigated the generation of acetylperoxy radicals ($CH_3C(O)O_2$) from the corresponding peroxynitrate according to the reversible reaction

$$CH_3C(O)O_2NO_2 \rightleftarrows CH_3C(O)O_2 + NO_2 \qquad (1,-1)$$

However, the alternative homolysis mechanism cannot be excluded on an a priori basis:

$$CH_3C(O)O_2NO_2 \rightarrow CH_3C(O)O + NO_3 \qquad (2)$$

In this report we demonstrate that reaction 1 is the predominant homolysis mechanism of peroxyacetyl nitrate (PAN). We also present our results on the use of PAN as a source of acetylperoxy radicals to determine the Arrhenius parameters for reaction −1 and for the reaction:

$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2 \qquad (3)$$

Estimation of the enthalpy changes for reactions 1 and 2 indicates that both reactions are endothermic by about the same amount, 26 ± 2 kcal/mol. However, the entropy changes are calculated to be considerably different: $\Delta S_1° = 42 \pm 2$ and $\Delta S_2° = 30 \pm 2$ cal deg^{-1} mol^{-1} (1 atm standard state). By analogy with other homolysis reactions, these entropy changes suggest a frequency factor of 10^{16} s^{-1} or greater for reaction 1 and about 10^{14} s^{-1} for reaction 2.[3] Therefore, reaction 1 would be expected to be considerably faster than reaction 2 (independent of temperature) if they do truly have similar heats of reaction.

To determine if the equilibrium in reaction 1 is important, we investigated the exchange of $^{15}NO_2$ with PAN at 25 °C, using an IR technique. To minimize decomposition of PAN on the walls of the cell, it was necessary to expose the reaction cell to PAN until a constant rate of disappearance of PAN was obtained (~1%/h). The conversion of unlabeled PAN to ^{15}N-labeled PAN (PAN-15) was followed by the decrease of the 1735-cm^{-1} band characteristic of unlabeled PAN[4] and the appearance of the 1696-cm^{-1} band characteristic of PAN-15.[5] Similarly the bands at 1590 and 1570 cm^{-1} from $^{15}NO_2$ were replaced by bands at 1618 and 1600 cm^{-1}, which are indicative of natural NO_2.[6] The expression for the loss of PAN in the case