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EXCIMER LASER FRAGMENTATION STUDIES OF SELECTED OXIMES: NASCENT OH INTERNAL ENERGY DISTRIBUTIONS AND THE SEARCH OF H_2CN FLUORESCENCE

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Excimer laser excitation (193 nm) of formaldoxime (H_2CN-OH) or the methylated homologs, R_1R_2CN-OH where R_1, R_2 = H or CH_3, results in dissociation. The upper limit for the quantum yield of fluorescence of the R_1R_2CN is estimated to be between 1-10% depending on the precursor used. The OH companion radical was probed by laser induced fluorescence (LIF) utilizing the A-X (2-1) and (1,0) bands near 34700 cm^{-1}, and the nascent rotational, vibrational, and ground electronic state spin-orbit distributions determined. No laser induced fluorescence of the R_1R_2CN radical could be observed upon irradiation in the regions where the radicals are known to absorb, 280 to 295 nm. From the nascent OH product distributions, we calculate that only 2.5 Kcal/mole of the excess energy appears as OH product internal energy, thus leaving about 80 Kcal/mole to be divided between the R_1R_2CN fragment and translation. We, therefore, conclude that it is highly likely that the upper states of these radicals probed in the 280 to 295 nm region are predissociative.

14. SUBJECT TERMS

Excimer Laser, Formaldoxime, Methyleneamidogen, Laser-Induced, Fluorescence, Spin-Orbit, Hydroxyl, Formaldazine, Acetaldoxime, Dissociation-Energy, Electronic State

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I. INTRODUCTION

There has been considerable interest in the development of sensitive laser spectroscopic probes for the detection of trace transient species in combustion environments.[1,2] Laser-induced fluorescence has been utilized for the observation of a number of free radical combustion species.[3] In this paper, we describe our attempt to observe laser-induced fluorescence of the methyleneamidogen radical, H_2CN, which is prepared by excimer laser photodissociation of formaldoxime [H_2CNOH]. We have also investigated the photodissociation of the methylated homologs of formaldoxime, namely acetaldoxime [CH_3CHNOH] and acetoxime [$(CH_3)_2CNOH$]. We also report the internal state distribution of the companion photofragment, hydroxyl, for these three precursors.

Methyleneamidogen was first observed by Cochran, et al.,[4] by ESR spectroscopy in an argon matrix and has been observed in other experiments by the same technique.[5-9] The ultraviolet absorption spectrum of H_2CN was first observed through flash photolysis of formaldazine [$(H_2CN)_2$][10-12] and subsequently in the photolysis of formaldoxime.[13] The observation of the same bands from these two precursors supported their assignment to H_2CN, and deuterium-substitution studies confirmed the presence of two hydrogen atoms in the molecule.[10] No rotational structure could be resolved in these bands. Recently, the infrared spectra of H_2CN and its deuterated counterparts have been observed by Jacox in an argon matrix.[14] All the vibrational bands have been assigned. The ultraviolet absorption spectrum was also observed, with only a small matrix shift. The methylated homologs of methyleneamidogen, namely CH_3CHN and $(CH_3)_2CN$, were also observed in the gas phase by flash photolysis, in this case, of the precursors acetaldazine [$(CN_3CHN)_2$] and dimethylketazine [$((CH_3)_2CN)_2$].[12]

Methyleneamidogen is believed to be formed in the early stages of the decomposition of nitramines, a class of important high-energy molecules.[15,16] Using ESR spectroscopy, Morgan and Beyer[9] observed H_2CN, along with nitrogen dioxide, as one of the species present in the vapors produced by the slow pyrolysis of cyclotetramethylenetetranitramine (HMX) near its melting point. The electron spin resonance spectrum they obtained for the matrix-deposited vapors from this pyrolysis was essentially identical to spectra of H_2CN obtained by other methods.[4-8] This transient molecule is also believed to be formed by the dissociation of methylenenitramine [CH_2NNO_2], which has been experimentally identified as a primary decomposition product in the molecular beam infrared multiphoton dissociation of cyclotrimethylenetrinitramine (RDX).[17] Methyleneamidogen may also be important as an intermediate in the reaction of hydrogen atoms with HCN.[18]

Further studies of the role of methyleneamidogen in nitramine decomposition would clearly benefit from a sensitive diagnostic tool for the detection of this species. The most prominent features in its electronic absorption spectrum occur near 280 nm.[10-13] There actually appear to be two electronic transitions occurring in this spectral region.[11,19] Quantum chemical calculations have also been carried out in order to estimate vertical excitation energies.[19] These calculations give a reasonable explanation of the electronic spectrum of this radical and provide assignments for the electronic states involved in the bands near 280 nm.

In this paper, we report a search for laser induced-fluorescence of methyleneamidogen and its methylated homologs upon excitation of the bands previously observed by flash photolysis. In view of the fact that no rotational structure was observed using a 10.7 meter spectrograph with 0.3 cm^{-1} spectral resolution,[11] the excited states of H_2CN may in fact be predissociated. Jacox[14] observed that the ultraviolet absorptions of a matrix-isolated sample decreased upon exposure to light from a medium-pressure mercury arc, while they remained unchanged when the sample was irradiated with light from an arc of wavelengths greater than 280 nm. If the excited state were strongly predissociated, it would, of course, lead to a negligible fluorescence quantum yield. It is interesting in this regard to make the comparison with the isoelectronic formyl radical, HCO. Most of the excited levels of HCO are diffuse, except for those with K'=0.[20] A laser optogalvanic study[21] revealed, in fact, a strong variation of the linewidth in the $\tilde{A}^2A''$ (0,9,0) K'=0 manifold. In spite of this predissociation, HCO has been successfully detected by fluorescence excitation in the $\tilde{A}^2A''$ (0,9,0)-$\tilde{X}^2A'$ (0,0,0) band.[22,23] More recently, the formyl radical has been detected in both a cell[24] and in a flame[25] by two-photon-resonant multiphoton ionization near 390-400 nm via its 3s and 3p Rydberg states. In view of the importance of developing a diagnostic for H_2CN, it was deemed worthwhile to investigate whether fluorescence could be observed with this molecule upon excitation of its known ultraviolet band systems.

We have chosen in this study to prepare methyleneamidogen by excimer laser photolysis of formaldoxime since the other photofragment is the hydroxyl radical, which is easily detected by fluorescence excitation. Formaldoxime exists at room temperature as a polymer and must be heated to produce the monomeric vapor.[26] Detection of the hydroxyl radical allows indirect verification of the presence of the oxime precursor and also provides a way to estimate our detection sensitivity for methyleneamidogen. Because of the difficulty in producing formaldoxime vapor, we have also investigated the photodissociation of its methylated homologs, acetaldoxime [CH_3CHNOH] and acetoxime [$(CH_3)_2CNOH$]. These precursors are expected to yield CH_3CHCN and $(CH_3)_2CN$, whose absorption spectra have been previously observed by flash photolysis of the corresponding azines.[12] These molecules were also investigated in the hope that their predissociation rate may be significantly less than that of H_2CN. Finally, the photodissociation of formaldazine and acetaldazine was also briefly studied.

II. EXPERIMENTAL SECTION

These experiments were carried out in a large vacuum chamber normally used for molecular beam scattering studies.[27] The photolysis source was an excimer laser (Lambda Physik EMG101MSC) usually operated at 193 nm with ArF; typical pulse energies of the unpolarized output were 10-20 mJ in a 1 cm x 3 cm rectangular area at the photolysis zone. A few experiments with acetaldazine precursor were carried out at 248 nm with KrF. The tunable ultraviolet probe laser beam, obtained by frequency doubling the output of a Nd:YAG pumped dye laser (Quantel), crossed at right angles to the excimer laser beam along the long dimension. Typical probe pulse energies at the apparatus were 200 μJ in a 4 mm diameter beam for laser fluorescence detection of OH in the $A^2\Sigma^+ - X^2\Pi$ (1,0) and (2,1) bands at 280-290 nm. Slightly higher power (500-800 μJ) was employed in the search for fluorescence from H_2CN and its homologs. Fluorescence detection of CN through excitation of its $B^2\Sigma^+ - X^2\Sigma^+$ (0,0) band near 388 nm was accomplished by mixing the dye laser output with the residual 1.06 μm Nd:YAG fundamental. The incident pulse energy of the probe radiation was approximately 100 μJ.

Fluorescence excited by the probe laser was collected with a 3-lens telescope and was detected with a photomultiplier (EMI 9813QB), whose output was directed to a gated integrator (Stanford Research Systems). For experimental convenience, the fluorescence telescope has a 90° bend in it. To reduce the scattered light background, a dichroic mirror, with reflectivity peaked over 300-350 nm, was used to make this bend. Below 300 nm, the reflectivity dropped rapidly, reaching 50% at 285 nm. For fluorescence detection of CN, the dichroic mirror was replaced with an aluminized one, and excimer laser scattered light was eliminated with the insertion of a 390 nm center wavelength, 10 nm FWHM filter. In many runs, excitation spectra were acquired under computer control (DEC LSIP-11/23), and the spectra were stored on magnetic diskettes for later analysis on another laboratory computer (Apple Macintosh).

The precursors acetaldoxime and acetoxime were obtained from Aldrich Chemicals. The stated purities were 95 and 98%, respectively. Acetaldazine was synthesized by the reaction of acetaldehyde and hydrazine hydrate according to the procedure of Curtius and Zinkeisen.[28] Checks of the infrared and mass spectra against literature infrared[29] and mass[30] spectra were made to insure the identity of the product. The purity of the product was found to be >98%.

Formaldazine polymer was prepared simply by the addition of formaldehyde to hydrazine hydrate using the procedure of Pulvermacher.[31] The alternative procedure of Hofmann and Storm[32] yields a ring compound, tetraformaltrisazine, $C_4H_{12}N_6$, rather than the desired polymer of formula $(C_2H_4N_2)_n$.[33] A check of the elemental composition (analytical physical measurements performed by E.I. duPont de Nemours and Company) of our product showed the correct elemental stoichiometry. An infrared spectrum of the polymeric sample was also taken and, in general, agreed with literature spectra of the monomer deposited in a low-temperature matrix.[34,35]

Formaldoxime was synthesized by the procedure of Scholl.[26] The identity and purity of the solid product was checked by infrared and gas chromatograph/mass spectra. Unfortunately, the only infrared spectrum available in the literature is for the gas phase monomer.[36] Also, no literature mass spectrum could be found. However, our observed mass spectrum exhibits approximately the fragmentation pattern expected for H_2CNOH, and the physical properties match known values.

Two types of photodissociation experiments were carried out for the study of both nascent and thermalized products. In the former, the vacuum chamber was evacuated with a baffled diffusion pump. Typical pressures for the precursors were 2-5 mTorr, with pump/probe delays of 2-4 μsec. For the study of thermalized products, the chamber was evacuated with a roughing pump, and nitrogen was added to give a total pressure of 0.6-1 Torr; pump/probe delays were 4-50 μsec and usually greater than 20 μsec.

Acetaldoxime, acetoxime, and acetaldazine, which are monomeric precursors, were admitted into the vacuum chamber by means of a needle valve on an evacuated flask containing the degassed material. Under normal conditions (298 K and 1 atm), formaldazine exists as a solid polymer, while formaldoxime is a solid trimer. In our first experiments, the desired monomeric precursors were obtained by depolymerization of the solids in a heated crucible located just under the photolysis/detection zone. This arrangement generated a significant amount of particulate material, which led to laser scattering that interfered with the taking of laser fluorescence excitation spectra. The problem was exacerbated when an inert diluent was added to the chamber (even at only 1 Torr pressure) because the buoyancy of the diluent gas caused a large amount of particulates to float in the laser beams, or the condensation rates of the generated vapors were affected.

To avoid the light scattering problem, we first attempted to make monomeric formaldoxime liquid, as has been done before.[13,26,36] We found that the best way to handle the gaseous formaldoxime monomer was to depolymerize the solid polymer in a test tube and inject it directly through a long, mildly heated section of metal tubing directly into the photolysis chamber. This procedure avoids the formation of particulates in the chamber. Also, there is very little decomposition because the temperature required is much lower than for formation of the liquid. We found that a depolymerization temperature of 80-90°C produced a pressure of several mTorr in the chamber with the pumps on. This is an adequate amount to perform photolysis experiments.

We did not devise a very satisfactory technique to inject formaldazine monomer into the chamber. Use of a technique similar to that which worked well for formaldoxime (depolymerization in a heated sidearm to the chamber) was thought to be difficult because the depolymerization temperature (ca. 200-220°C[10,11]) is high enough to cause materials problems since the heated components would be exposed to room air. However, in retrospect, this technique might work well because a lower temperature might still be sufficient to produce several mTorr of monomer. (Lower pressures of monomer are required in these experiments than were used in the flash photolysis experiments.[10-14]) In any case, it is clearly probable that the formaldazine monomer could be produced nicely in the photolysis chamber by heating a sidearm contained under vacuum. Such apparatus was not readily available to us. Therefore, most of the experiments on azines were performed with acetaldazine.

III. RESULTS AND DISCUSSION

A. Fragmentation Energetics

There is considerable uncertainty in the R_1R_2CN-OH bond dissociation energy for the oximes. The bond dissociation energy for formaldoxime ($R_1 = R_2 = H$) can be estimated by using its heat of formation ($\Delta H^0_{f298} = 0$ kcal/mole) derived from bond additivity considerations by Benson and O'Neal[37] and the H-HCN binding energy (19 kcal/mole) calculated by Bair and Dunning[18] for the H_2CN species. With the aid of the well-determined heats of formation of H and HCN,[38] we estimate a bond energy of 74 kcal/mole for formaldoxime. The Bond-Additivity-Corrected Moller-Plesset fourth order perturbation theory (BAC-MP4) method has been used to calculate the thermochemistry of a number of combustion species.[16] Using the BAC-MP4 values[39] for ΔH^0_{f298} of H_2CNOH and

H_2CN (5.1 and 58.9 kcal/ mole, respectively), we obtain a H_2CN-OH bond energy of 63.0 kcal/mole, which is in moderate agreement with the previous cruder estimate.

We would expect methylation not to change drastically the R_1R_2CN-OH bond energy. Benson and O'Neal[37] estimated a value of 48.4 kcal/mole for acetaldoxime ($R_1 = CH_3$, $R_2 = H$) from available experimental unimolecular decay kinetic data. This value seems quite low in light of the estimates for formaldoxime. Indeed, Benson and O'Neal questioned the validity of the experimental data. We can obtain another value using their estimated[37] ΔH^0_{f298} for acetaldoxime (-7.3 kcal/mole) and a BAC-MP4 value[39] for CH_3CHN (50.1 kcal/ mole). We obtain a $CH_3CHN-OH$ bond energy of 66.6 kcal/mole, which is quite similar to that for formaldoxime. At present, there is no information on acetoxime ($R_1 = R_2 = CH_3$); however, we expect a similar bond energy.

The ultraviolet spectra of the oximes contain two absorption regions, a weak diffuse band near 210-213 nm and an intense band with a maximum below 190 nm.[11] Accordingly, our photodissociation studies were carried out only with an ArF excimer laser (193 nm) as the photolysis light source. This implies that there is approximately 85 kcal/mole of energy available to the photofragments, if a R_1R_2CN-OH bond energy of 63 kcal/mole is assumed.

B. OH Fragment Internal State Distributions

The OH product was observed by laser fluorescence excitation in the $A^2\Sigma^+ - X^2\Pi$ (1,0) and (2,1) bands. These particular bands were chosen since they lie very close to the wavelengths of the absorptions previously observed for H_2CN and its homologs. The dependence of the OH fluorescence signals for several lines was investigated as a function of excimer laser pulse energy. On a log-log plot the slope was found to equal 1.25 ± 0.1. This is roughly consistent with a one-photon photodissociation process. Under thermalized conditions, the OH fluorescence signal decreased with a half life of approximately 100 μsec with respect to the pump/probe delay in 0.7 Torr nitrogen buffer gas. This is comparable with the expected diffusion time out of the photolysis zone.

The OH(v=0) rotational distributions were taken from (1,0) R_1 and R_2 branch intensities. The intensities were converted to rotational populations using fluorescence excitation line strength factors calculated by the formulas of Greene and Zare.[40] It was assumed that the OH photofragments had an isotropic M_J distribution. The nascent distributions, which are plotted in Figure 1, were found to be somewhat hotter than for thermalized samples. The distributions are essentially identical for all three oxime precursors and exhibit a preference for production of the $F_1(\Omega = 3/2)$ over the F_2 $(\Omega = 1/2)$ spin-orbit component, particularly at low N.

The OH(v=1)/OH(v=0) population ratio was also estimated for acetaldoxime precursor since high-N P_1 and P_2 lines of the (1,0) band overlapped the (2,1) band origin, as shown in Figure 2. We estimate that the nascent $v = 1$ to $v = 0$ ratio equals 0.02 ± 0.01. In deriving this ratio, a correction for predissociation[41,42] of the low N levels of v'=2 was made. From the measured OH internal state distribution, we conclude that an average of only 2.5 kcal/ mole appears as excitation of the OH fragments for acetaldoxime precursor. Similar results apply to formaldoxime and acetoxime. Thus, the overwhelming majority of the energy available to the fragments must be present as translational recoil and internal excitation of the R_1R_2CN fragment.

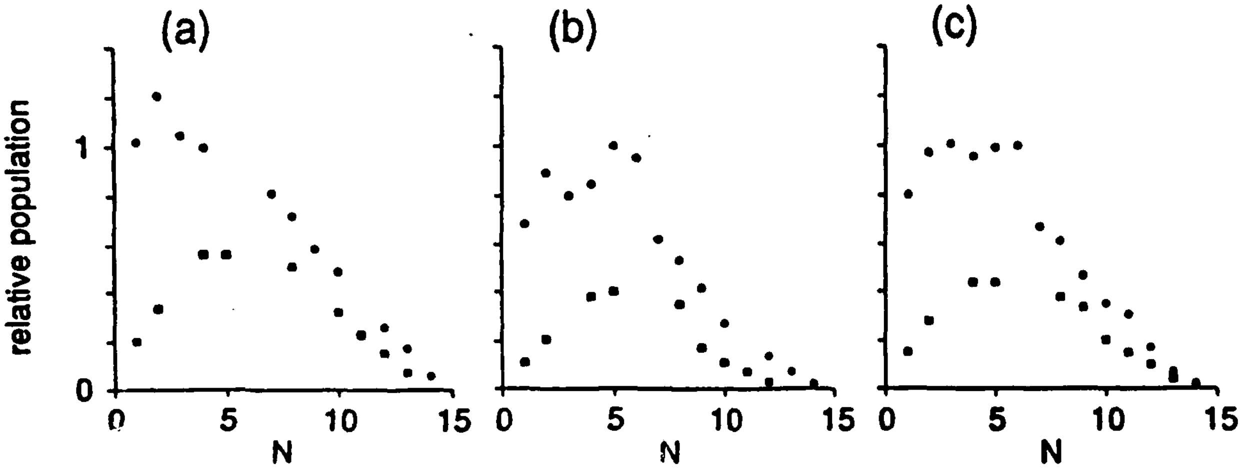

Figure 1. Rotational State Populations for OH (v=0) Produced in the 193-nm Photodissociation of (a) Formaldoxime, (b) Acetaldoxime, and (c) Acetoxime. The circles and squares represent the $F_1(\Omega=3/2)$ and $F_2(\Omega=1/2)$ spin-orbit levels, respectively. The distributions are each separately normalized to a particular F_1 level. The populations are not divided by the (2J+1) degeneracy factor.

C. Search for H_2CN Fluorescence

With OH detected as a photofragment from the oximes, it can be assumed that H_2CN, or its homologs, will be present in the photolysis at the same concentration as OH if no subsequent excimer-laser-induced decomposition or reactions of R_1R_2CN occur. (In Section D, we address the possibility that this assumption may not be correct.) Extensive searches for laser fluorescence signals from H_2CN and its homologs were carried out, both under nascent and thermalized conditions. No fluorescence signals attributable to these species could be found. For the formaldoxime precursor, scans were taken over 280-286 nm in the region of the strongest absorption bands seen in the flash photolysis experiments on formaldoxime[10,11,13] and formaldazine.[12] Because of the ease of introducing the precursor into the apparatus, the photolysis of acetaldoxime and acetoxime were more extensively studied. For these molecules, scans were taken over the range 287-295 nm in the regions where CH_3CHN and $(CH_3)_2CN$ have been found to absorb.[12]

From our lack of observation of R_1R_2CN fluorescence and our observed signal-to-noise ratio for OH lines, we can estimate an upper limit to the R_1R_2CN fluorescence quantum yield, provided we assume that the concentrations of R_1R_2CN and OH are equal in the photolysis zone. Ogilvie and Horne[10] have estimated the integrated oscillator strength for the 280 nm band of H_2CN to be $(4\pm2) \times 10^{-4}$. We shall assume that the oscillator strength of the corresponding bands in the radicals produced from acetaldoxime and acetoxime are similar. Since the band is approximately 200 cm^{-1} wide, this implies an average oscillator strength per unit bandwidth of $2 \times 10^{-6}/cm^{-1}$. We can estimate the oscillator strengths of the OH (1,0) and (2,1) bands from the known radiative lifetimes and fluorescence branching ratios:[43-46] $f_{1,0} = 3.1 \times 10^{-4}$ and $f_{2,1} = 4.5 \times 10^{-4}$.

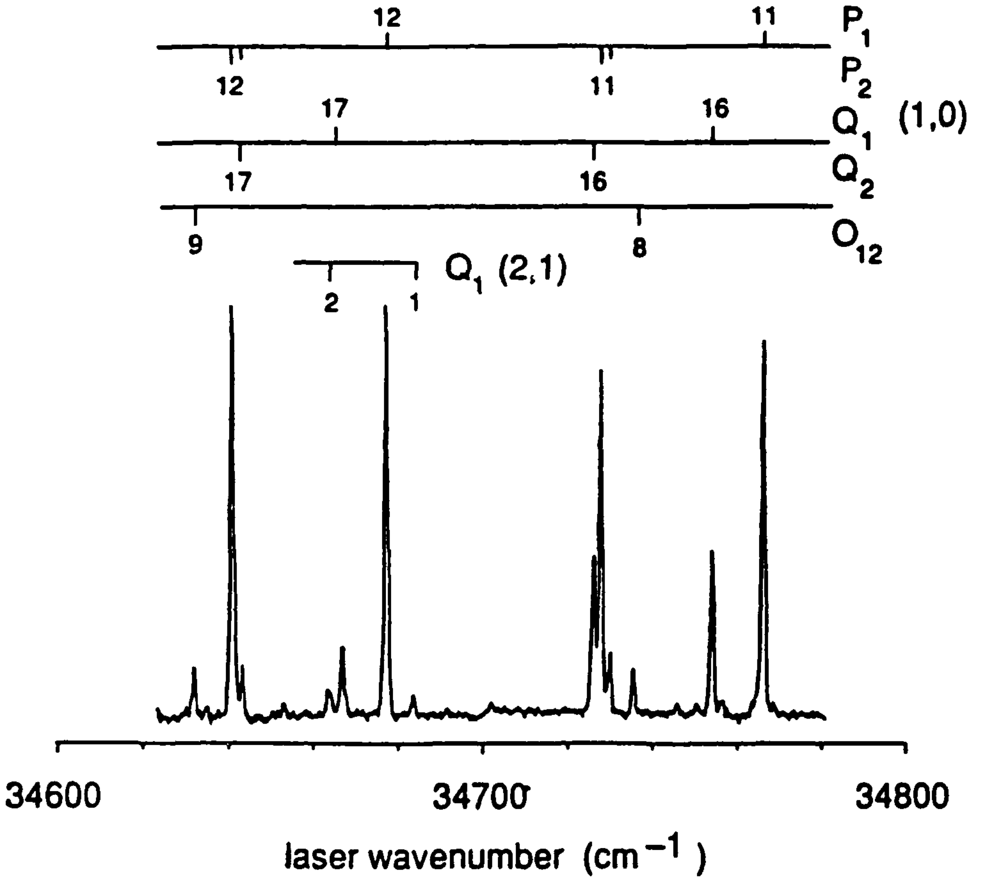

Figure 2. Excitation Spectrum Near the OH A-X (2,1) Band Origin for Photodissociation of Acetaldoxime Under Nascent Conditions. Lines of the (1,0) band and of the (2,1) Q_1 branch are marked. The pressure and pump/probe delay were 4 mTorr and 3 μs, respectively.

Our most sensitive searches for R_1R_2CN fluorescence were carried out with acetaldoxime and acetoxime and with nitrogen added as a thermalizing buffer. Under these conditions, lines in the OH (2,1) band could be observed with signal-to-noise ratio of greater than 100 in some scans. The oscillator strengths given in the previous paragraph and the previously determined OH ($v=1$) to ($v=0$) population ratio imply that the ratio of an R_1R_2CN signal to that of a low N line in the OH (2,1) band should equal approximately unity if the fluorescence quantum yield Φ of R_1R_2CN were unity, assuming also that the quantum yield for OH excited fluorescence is also unity. This suggests that Φ is less than 1% for CH_3CHCN and $(CH_3)_2CN$.

The N_2 pressure and delay time of these scans were sufficiently low to prevent vibrational relaxation[47] in the $OH(X^2\Pi)$ state. In fact, the zero-pressure fluorescence quantum yield for OH $v'=2$ is considerably less than unity because of predissociation.[41,42] The measured radiative lifetime (ca. 450 nsec, which is significantly longer than the lifetime of low N levels in $v'=2$ under collision-free conditions[41,42]) of the laser excited OH ($v'=2$) indicated that vibrational relaxation[48] to the nonpredissociating lower vibrational levels was occurring in the $A^2\Sigma^+$ state; this would have the effect of substantially raising the fluorescence quantum yield over that for $v'=2$ in the absence of collisions.[41,42] Our estimate for the upper bound on Φ would be even further reduced if the quantum yield of OH fluorescence were less than unity. Hence, we conclude Φ is certainly less than 1% for CH_3CHCN and $(CH_3)_2CN$. The derived upper limit for Φ is approximately one order of magnitude larger for H_2CN since the OH signals observed for formaldoxime precursor were smaller.

While not observing fluorescence attributable to R_1R_2CN, we did observe weak fluorescence from an as yet unidentifiable species other than OH. Figure 3 shows an excitation spectrum of a thermalized sample of photolyzed acetaldoxime in the region of the OH (2,1) band head. In contrast to the nascent spectrum in Figure 2, the high N lines of the OH (1,0) band are very weak compared to those of the (2,1) band because of rotational relaxation in $v''=1$. In addition to the strong OH lines, we can see a weak set of lines with closer spacing which appear to be converging to a band head degraded to the red near 34650 cm^{-1}. In addition to these lines, a second set of more closely spaced lines were observed around 34150 cm^{-1}, as shown in Figure 4. The spacing between lines in the latter region is much smaller than in the former.

We do not believe that these lines are due to R_1R_2CN since (1) they do not match the wavelengths reported for R_1R_2CN from the flash photolysis studies and, more importantly, (2) they appear at identical wavelengths with acetoxime as the precursor. (The lines near 34650 cm^{-1} also appeared, weakly, with formaldoxime.) In an attempt to identify the molecular carrier of these lines, we measured the radiative lifetimes of several of the lines. We estimate the fluorescence decay lifetime to be approximately 1 μsec, roughly independent of the line excited and the nitrogen pressure over 0.3-1 Torr. The precision of our measurement is poor because the signal is small compared with the probe laser scattered light. One possible candidate for the molecular species is methoxy, CH_3O, which does have bands in this region[49] and whose radiative lifetime is reported to be 1.5 μsec.[50] However, the rotational structure for a room-temperature sample of methoxy would be expected to be much more dense than the spectra shown in Figures 3 and 4.

At present, we do not have a suitable candidate species to attribute to these bands. We do, however, have several comments to make about the bands. Firstly, there is so much interference from the strong OH lines obscuring the short wavelength, better resolved band that it is difficult even to attempt to fit the rotational structure of the band. The OH lines make it particularly difficult to observe the band origin which would facilitate fitting the spectrum. Secondly, the splitting between the two bands is about 450 cm^{-1}.

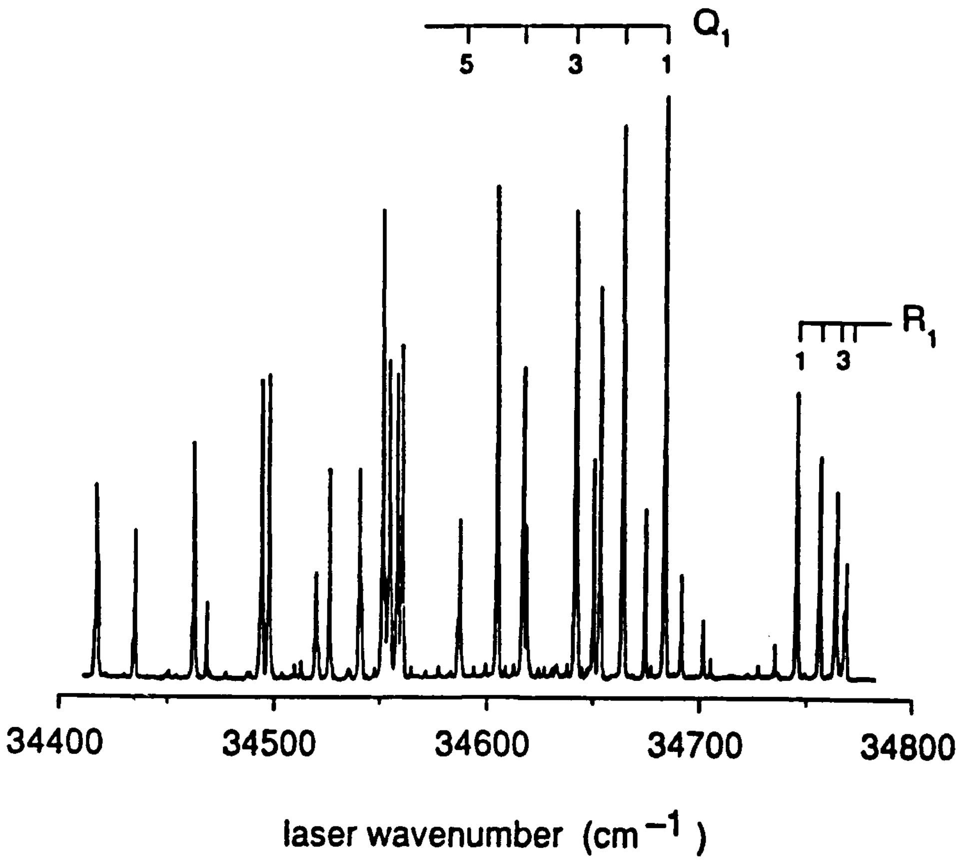

Figure 3. Excitation Spectrum Near the OH A-X (2,1) Band Origin for Photodissociation of Acetaldoxime Under Thermalized Conditions. All the strong lines are due to OH. The Q_1 and R_1 branches of the (2,1) band are marked. The splitting of the R_1 branch lines is due to strong satellite transitions near the main branch lines for these low N values. The pressure and pump-probe delay were 0.66 Torr (nitrogen added) and 25 μs, respectively.

This mitigates against the possibility that the two bands are subbands of the same vibrational band resulting from spin-orbit splitting because the splitting is so large. If the two bands belong to the same molecule, it would therefore seem that they are different vibrational bands. The form of the short wavelength bands appears to be much simpler than the long wavelength band. The former may consist of only P and R branches, with no apparent spin splitting, while the latter apparently has more branches. If the bands arise from the same molecular species, it therefore seems likely that the vibrational symmetries of the levels involved in the two bands are different. Alternatively, there could be a K' dependent predissociation in the short wavelength band, as in the HCO $\tilde{A}^2A''-\tilde{X}^2A'$ spectrum.[20,21]

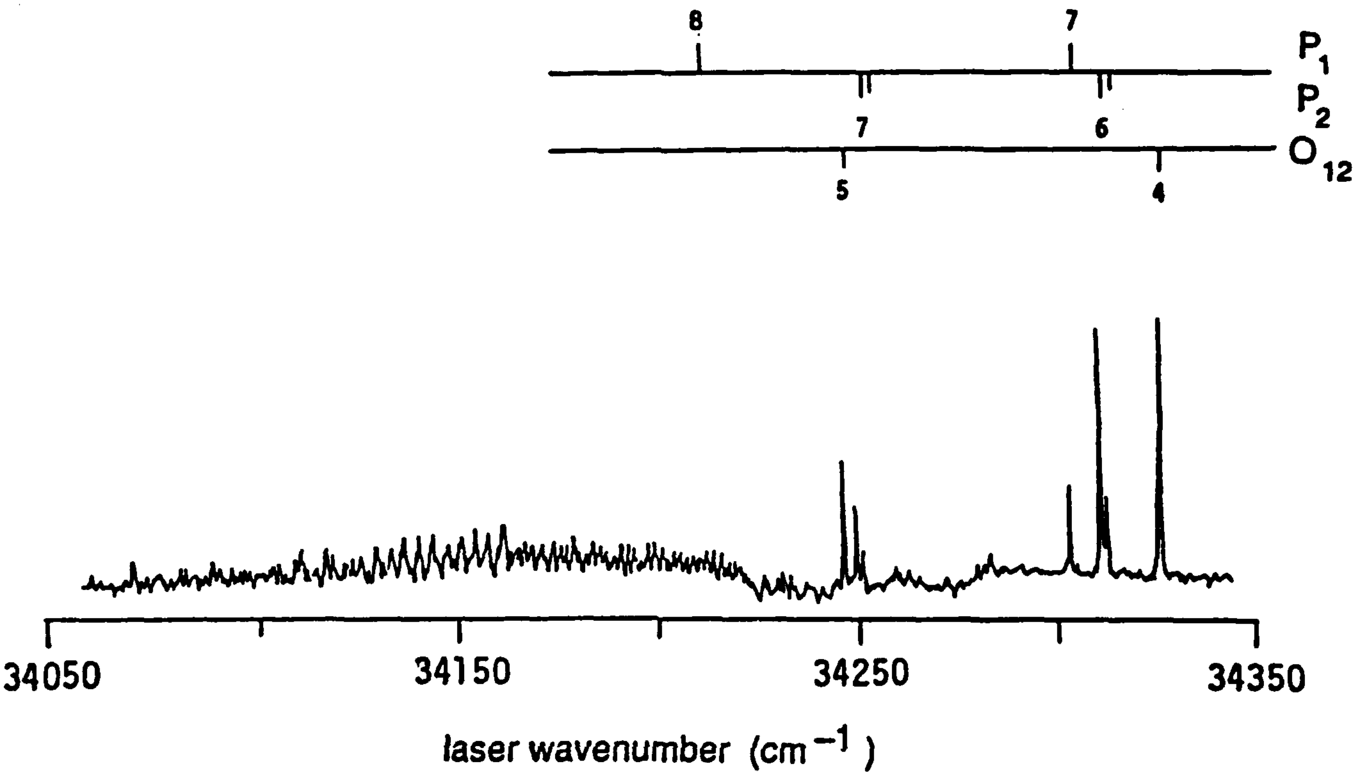

Figure 4. Excitation Spectrum Around 34150 cm^{-1} for Photodissociation of Acetaldoxime Under Thermalized Conditions, Showing a Band of an Unidentified Species. Lines of the OH A-X (2,1) band are marked.

We also investigated the 193 nm photolysis of formaldazine and the 193 and 248 nm photolysis of acetaldazine. No fluorescence signals attributable to any molecular species were observed with the probe laser tuned through the wavelength regions where the appropriate R_1R_2CN fragments are known to absorb.[10-13] The sensitivity of these runs was less than those with oxime precursors. Moreover, our detection sensitivity could not be calibrated in situ since, of course, no OH is produced by the photolysis of these compounds.

D. Detection of CN

In estimating the upper bound to Φ, it is possible that our assumption of equal concentrations of the OH and R_1R_2CN photofragments may not be correct. The flash photolysis work[10-13] suggests that the latter is not rapidly consumed by chemical reactions since the R_1R_2CN absorptions were seen to persist at much higher reactant pressures than used in the present work for at least 80 μsec. However, in our experiments, it is possible, at least in .

principle, that R_1R_2CN could itself be destroyed in the initial photodissociation since the energy available to the fragments considerably exceeds the R_1-R_2CN bond energy (see Section A) and only a small fraction of this energy appears as OH excitation (see Section B). Thus, both R_1R_2CN + OH and R_1CN + R_2 + OH photolysis products could be formed in a one-photon process. The dissociation wavelength in the present experiment (193 nm) is somewhat shorter than in the flash photolysis studies since the Kr flashlamp output there dropped rapidly below 200 nm.[12] The effective wavelength range of the photolysis radiation is actually a convolution of the flashlamp output and the oxime absorption coefficient, which is rapidly rising below 200 nm. Hence, it is possible that fragmentation of R_1R_2CN is more likely with photolysis using 193 nm radiation, than with a Kr flashlamp. In fact, the appearance of successive absorption maxima in the continuum spectra of both the oxime and azine precursors[10,12,13] as one goes toward shorter wavelengths may indicate the onset of some fraction of higher fragmentation photolysis.

In an effort to determine the importance of such destruction of R_1R_2CN, we looked for production of CN by laser fluorescence excitation. Indeed, we observed CN through fluorescence excitation in its $B^2\Sigma^+ - X^2\Sigma^+$ (0,0) band upon 193 nm photolysis of acetaldoxime. No attempt was made to measure quantitatively the CN concentration relative to that of OH because of the widely different wavelength range, and laser and filter bandwidths. However, we estimate that the CN concentration was significantly less than that of OH since comparable photomultiplier signals were observed; the oscillator strength of the CN B-X (0,0) band equals $(3.11 \pm 0.05) \times 10^{-2}$ [51] and is hence much larger than for the OH ($\Delta v=+1$) sequence. The dependence of the CN fluorescence signal was investigated for several lines as a function of excimer laser pulse energy under thermalizing conditions (1.0 Torr nitrogen added, 4 μsec pump/probe delay). On a log-log plot, the slope was found to equal 0.78 ± 0.1. This suggests that CN is formed by a one-photon dissociation process from the oxime. The process $CH_3CHNOH \rightarrow CH_4 + CN + OH$ requires approximately 110 kcal/mole. This dissociation pathway is clearly feasible in a one-photon process at 193 nm.

In addition to the observation of ground state CN by laser fluorescence detection, an emission signal coincident with the ArF excimer laser pulse was seen through the 390 nm bandpass filter with the acetaldoxime precursor. We do not believe this is due to direct photolytic production of $CN(B^2\Sigma^+)$ because the decay time of this signal (ca. 1 μsec) is much longer than the CN(B) radiative lifetime (ca. 70 nsec[51]). The dependence of the emission signal on the excimer pulse energy was found to be approximately linear (slope of 0.99 ± 0.1 on a log-log plot). However, production of CN(B) in a one-photon process at 193 nm is not energetically allowed. Unfortunately, it was not possible in the present apparatus to take a spectrum of this emission, thus elucidating the species responsible.

IV. CONCLUSION

In this work, we have investigated the 193 nm photodissociation of the simplest oximes, namely formaldoxime, acetaldoxime, and acetoxime. The OH photofragment was detected, and its internal state distribution determined. An unsuccessful search was made to observe laser excited fluorescence from the other photofragment R_1R_2CN, where R_1 and R_2 equals H or CH_3. Based on the assumption of an equal concentration of OH and R_1R_2CN upon photolysis of the oxime, we were able to estimate a rough upper bound of 1% for the fluorescence quantum yield Φ of the R_1R_2CN absorption bands in the 280-295 nm region. This implies that electronic states excited in these transitions are predissociative. Through the detection of CN, there is some evidence that the R_1R_2CN is itself destroyed to some extent in the initial event of the 193 nm photodissociation of the oxime. This could have the effect of increasing our estimate on the upper bound to Φ.

The present study indicates that fluorescence excitation of the electronic bands near 280 nm of methyleneamidogen is not a feasible laser diagnostic for this species. The infrared absorption bands of H_2CN, which have been identified in the recent matrix study of Jacox,[14] may have utility as a probe for this molecule. An alternative, more sensitive technique may be resonant-enhanced multiphoton ionization through a Rydberg state, as has been successfully carried out for HCO.[24,25]

Recently, Marston, et al.,[52] have shown that H_2CN can be produced in high yield from the $N + CH_3$ reaction. Using the discharge flow/mass spectrometry technique, this group has measured the elementary reaction rate constant for the $N + H_2CN$ reaction. These results imply that mass spectrometric detection of H_2CN may be a viable alternative diagnostic for this species. In addition, it would be interesting to compare the production of H_2CN by this chemical method with our photolytic approach.

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