Laser Photodissociation and Thermal Pyrolysis of Energetic Polymers

Ping Ling and Charles A. Wight*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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Decomposition reactions of glycidyl azide polymer (GAP) and poly(glycidyl nitrate) (PGN) have been investigated by pulsed infrared laser pyrolysis and ultraviolet laser photolysis of thin films at 17−77 K. Reactions are monitored by transmission FTIR spectroscopy. Photolysis of GAP at 266 nm shows that the initial reaction steps are elimination of molecular nitrogen with subsequent formation of imines. Warming leads to loss of the imines, most likely as a result of secondary polymerization reactions. Thermal decomposition of GAP by infrared laser pyrolysis reveals products similar to the UV experiments after warming. Laser pyrolysis of PGN indicated that the main steps of decomposition are elimination of NO_2 and CH_2O from the nitrate ester functional group, followed by rearrangement of the polymer backbone to form carbonyl functional groups. Higher order reactions form numerous small molecule products including NO, CO, CO_2, N_2O, H_2O, HNCO, HCN, HCNO, HONO, and CH_4. UV laser photolysis of PGN shows the major products to be CO, CO_2, N_2O, and polymeric carbonyls. A mechanism is suggested to account for the difference between products in the UV and infrared laser experiments. Quantum yields for destruction of the azide group in GAP and for destruction of the nitrate ester group in PGN are 8×10^{-3} and 1×10^{-3}, respectively, for 266 nm excitation.

Introduction

Glycidyl azide polymer (GAP) and poly(glycidyl nitrate) (PGN) are energetic polymers that have been proposed for use as binders in solid rocket motors. The un-cross-linked oligomers used in this study are viscous liquids at room temperature.
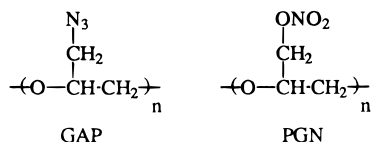
GAP and other azide-containing polymers have been the subject of several studies over the years. Brill and co-workers[1,2] found that GAP decomposes at about 250 °C during rapid heating; the major products are N_2, CO, HCN, NH_3, CH_2O, CH_4, C_2H_2, and C_2H_4. Thermal decomposition at high temperature and high pressure produces N_2, H_2, CO, C, and other minor products.[3] Although these studies have proved valuable for understanding the gas phase decomposition kinetics, it has been difficult to determine the initial steps of the decomposition mechanism because the time scale of reactions is short and the products are not usually detected in the condensed phase. Haas and co-workers[4] studied the thermal decomposition of GAP by pulsed CO_2 laser irradiation and found that both gaseous products and smoke powder are formed. The gaseous products are mainly N_2, CO, C_2H_4, HCN, CH_4, and C_2H_2. The smoke powder was assigned to be principally imines, as indicated by a broad infrared absorption band near 1650 cm^{-1}. However, early studies of methyl azide decomposition show that there are other strong bands associated with imines[5] that were not reported by Haas and co-workers, casting some doubt on this assignment.

Thermal decomposition of a series of nitrate esters was studied by Oxley and co-workers recently.[6] They concluded that the rate-determining step in nitrate ester thermolysis is usually homolytic cleavage of the RO−NO_2 bond. Chen and

Brill studied the thermal decomposition kinetics of PGN and found the reaction to be first-order for slow heating rates[7] but second-order for rapid heating.[8] Under rapid heating conditions, the gaseous decomposition products were determined to be CO, CO_2, NO, NO_2, H_2CO, HCN, HONO, and HCO_2H. However, the mechanism by which these products are formed is still not well established. In earlier work on nitrocellulose, Gelernter *et al.*[9] had proposed that rupture of NO_2 from the side chain is the first step of thermal decomposition. However, a more recent study suggested that the reaction begins with second-order reaction of nitrate ester groups.[10]

Recently, transient thin film laser pyrolysis techniques, which use CO_2 laser pyrolysis of target materials, following by rapid thermal quench of reaction products, has restricted reaction time at high temperatures to within a millisecond scale.[11] Just as shock heating is suitable for studying gaseous reactions at high temperatures for short periods, this technique has been proved successful in studying initial thermal reaction in the condensed phase.

Laser photolysis is also a useful tool in studying the decomposition mechanism of molecules. Although it is not likely to involve electronically excited states in normal thermal decomposition, it is suggested that electronic excited states may play an important role in detonation.[12] On the other hand, if internal conversion of electronically excited states to a vibrationally excited ground electronic state is important, then the photolytic decomposition product ratios should bear a strong similarity to those resulting from thermal decomposition.

Because GAP and PGN polymers have the same backbone structure, it is appropriate and helpful to use transient thin film laser pyrolysis and laser photolysis techniques to study initial reactions in both materials in one set of experiments.

Experimental Section

GAP was obtained from the 3M Company, which markets the material as an energetic binder for propellants. The material used in our study is the un-cross-linked polyol, which has a linear repeating structure but is synthesized using a branched

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initiator. PGN was supplied by Dr. Robert Wardle of Thiokol Corp. Both GAP and PGN are viscous liquids at room temperature.

Pulsed Infrared Laser Pyrolysis. The details of the apparatus have been described elsewhere.[11] Briefly, a thin film of GAP or PGN is sandwiched between two salt windows (CsI or CaF_2) and mounted at the cold tip of an evacuated liquid nitrogen Dewar vessel. The vacuum enclosure has two infrared windows mounted on opposite sides for obtaining transmission FTIR spectra and one or two quartz windows mounted on the two remaining sides of the cell for photolysis. The vacuum cell is pumped to 10^{-4} Torr; then the cold finger is cooled to 77 K by liquid nitrogen. In some experiments, the sample was cooled to 17 K by a closed cycle helium refrigerator in a similar vessel.

Pyrolysis of the sample is carried out by pulsed CO_2 laser irradiation (Pulse Systems Model LP140-G). The laser was tuned to 1039.5 cm^{-1}, and the pulse length is about 35 μs. The laser beam size can be adjusted by means of a spherical mirror and is measured by irradiating a target of thermally sensitive paper. The average energy per pulse is calculated from the beam power, as measured by a Scientech Model 38−0101 disk calorimeter. Typically, laser fluences in the range 0.5−2.3 J/cm^2 were used in these experiments.

Neither GAP nor PGN has any strong infrared absorption bands within the tuning range of the pulsed CO_2 laser (900−1100 cm^{-1}). Therefore, infrared laser pyrolysis experiments were conducted using two different methods. In the first method, we deposit a thin film of salt ($NaBF_4$, which has very strong absorption at the laser frequency) on the IR window prior to sample preparation. The salt film is in good contact with the GAP or PGN to ensure efficient thermal conduction during laser pyrolysis. The second method is to use a relatively thick sample of GAP or PGN (≥ 15 μm). Although the energy deposition per unit volume of sample is the same as for thin films, the rate of conduction out of the sample is much slower, so reactions have a greater time to take place. Usually in the first method, a single shot is enough to reach maximum concentration of reaction products, whereas the second method normally requires five to seven shots at the highest available fluence (2.3 J/cm^2) to achieve similar results.

Transmission FTIR spectra were recorded before and after pyrolysis by means of a Mattson Model Polaris FTIR spectrometer. Spectra are obtained by averaging 32 scans at 0.5 cm^{-1} resolution.

Pulsed UV Laser Pyrolysis. The sample assembly is the same as for laser pyrolysis. Before photolysis, the sample is turned to face one of the quartz windows. After photolysis, the sample is turned to face both IR windows before recording the infrared spectrum. Photolysis is carried out by using the fourth harmonic of a Nd:YAG laser (Continuum Model Surelite) at 266 nm. The laser pulse duration is 7 ns, and the laser power is typically 35 mW at 10 Hz repetition rate, as measured by the disk calorimeter. The spatial profile of the beam is determined by recording the laser power while a razor blade is scanned across the beam. The data are differentiated and fit to a Gaussian function to determine the $1/e$ diameter of the beam, which was determined to be 3.9 mm. A lens is used to expand the beam to the desired fluence, which was typically 1 mJ/cm^2 in this study. The bulk temperature change of the sample due to absorption of laser light is estimated not to exceed 1 K.[13]

Ordinary Thermal Decomposition Experiments. A drop of GAP or PGN is placed in a glass tube, and the tube is evacuated and sealed. The end of the tube with material inside is immersed in an oil bath at 170 °C for GAP or 160 °C for PGN. After about 30 min the evolved gas is admitted to an evacuated IR gas cell for detection. In some experiments the gas phase products were condensed onto a 17 K cold window in a deposition chamber for IR detection in the condensed phase. The pyrolysis temperatures were chosen as the lowest temperatures at which gas bubbles can be observed to evolve from the GAP or PGN.

At higher temperatures, it is easy to induce explosive thermal decomposition. For example, when a tube containing GAP is placed in a hot bath at 230 °C, an explosion occurs in seconds, and all of the GAP is consumed.

Supplementary Experiments. GAP exhibits weak absorption around 285 nm; this transition has been assigned to the $n-\pi*$ transitions in the azide functional groups.[14] Similarly, PGN exhibits a weak $n-\pi*$ absorption at 270 nm. The absorption cross sections at 266 nm were measured by a Hewlett-Packard diode array UV−visible to be 7.5×10^{-20} cm^2 and 8.8×10^{-20} cm^2 per functional group for GAP and PGN, respectively.

Calibration experiments were carried out in order to determine the relative integrated infrared absorption coefficients for CO, CO_2, N_2O, NO, NO_2, CH_2O, and some gas mixtures. Samples containing 1−10 μmol of the authentic compounds were deposited onto a 2.5 cm diameter infrared window at 17 K at a rate not exceeding 5 $\mu mol/min$. Formaldehyde was made by thermal depolymerization of paraformaldehyde; other gases were used as supplied from commercial sources. A good linear relationship was observed between the integrated absorption intensity and the amount of gas deposited. In most cases, the band positions and widths were somewhat dependent on temperature, but the integrated intensities were essentially constant. The exceptions were N_2O_3 and $(NO)_2$, for which some of the integrated intensity of some bands increased as much as 30% from 17 K to 77 K. In the case of NO and NO_2, the absorption coefficients were determined by depositing these samples as monomers in an excess of argon matrix gas. Annealing these samples to evaporate the argon component produced bands that have been assigned previously to the dimers[15] and (in the case of mixed NO/NO_2 samples) N_2O_3.[16] The integrated absorption coefficients (in cm/μmol) measured in this manner are given in Table 1.

Results

UV Laser Photolysis of GAP. Transmission FTIR spectra of thin films of GAP were obtained before and after UV laser photolysis, as illustrated in Figure 1a,b. After photolysis, the intensity of the characteristic azide band at 2100 cm^{-1} is greatly reduced compared with the other bands. New absorption bands

TABLE 1: Integrated Infrared Absorption Coefficients

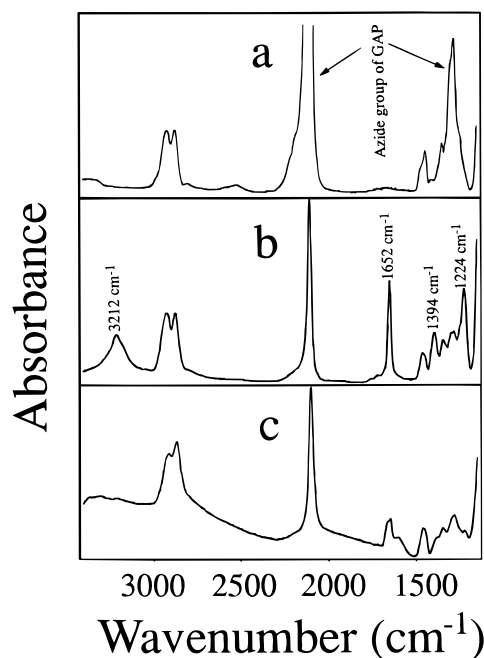| molecule	band position (cm^{-1})	integrated absorption coefficient (cm/μmol)
CO_2	2344	19.
CO	2138	2.3
N_2O	2238	13.
H_2CO	1720	2.8
	1495	1.2
$(NO)_2$	1861	0.93
	1755	4.5
N_2O_3	1861	6.4
	1594	5.1
	1300	4.2
	784	0.62
$(NO_2)_2$	1874	0.8
	1738	6.2
	1255	6.5
	747	2.2

Figure 1. Infrared spectrum of a GAP sample (a) prior to and (b) following 266 nm laser photolysis at 77 K. Spectrum c is the same sample after warming to room temperature for several hours.

appear at 3212, 1652, 1394, and 1224 cm^{-1}. The intensities of the new bands are highly correlated, suggesting that they come from the same products or group of products. It is noteworthy that absorption bands of GAP associated with C−O−C stretching vibrations (1082−1128 cm^{-1}) and C−H stretch vibrations (2750−3000 cm^{-1}) remain almost unchanged after photolysis. This suggests that the backbone of the polymer is rather stable with respect to 266 nm radiation. Photolysis for extended periods (i.e., until all the azide groups are destroyed) revealed a tiny infrared band due to CO, suggesting that only a tiny portion of backbone is broken to release CO.

A control experiment was carried out in which a sample of poly(propylene glycol) polymer was photolyzed for extended periods.

poly (propylene glycol)
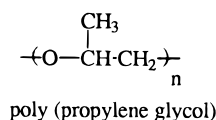
This polymer is similar to GAP except that the azide group is replaced by a hydrogen atom. No change in reactant bands was observed, and no products were formed.

When photolyzed samples are warmed to room temperature, additional changes occur over a time scale of several hours. The polymer undergoes a transformation from a transparent viscous liquid to a solid that is highly light scattering. The infrared spectra show that the bands at 3212, 1394, and 1224 cm^{-1} disappear completely, and the band at 1652 cm^{-1} broadens and diminishes in intensity, as shown in Figure 1c. The quantum yield for destruction of the azide group under 266 nm photolysis was measured by recording the integrated absorption intensity, A, of the azide band at 2102 cm^{-1} as a function of cumulative laser fluence, J (photons/cm^2). For optically thin samples, the quantum yield can be found from the relationship

$$\ln(A/A_0) = -\Phi\sigma J \qquad (1)$$

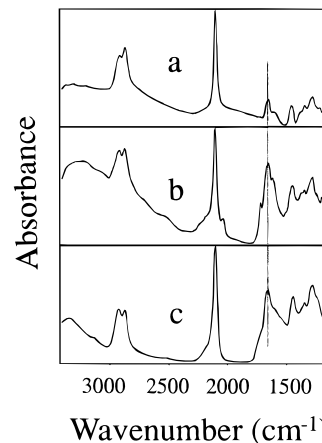where Φ is the quantum yield and σ is the measured 266 nm

Figure 2. Infrared spectra of GAP showing the similarity of samples that were (a) subjected to 266 nm laser pyrolysis and warmed to room temperature for several hours, (b) subjected to CO$_2$ laser pyrolysis at 77 K, and (c) a residue of a GAP film that was heated to 170 °C for 30 min.

absorption coefficient. A plot of $\ln(A/A_0)$ was found to be linear in J, and the resulting value of Φ determined from the slope is 8×10^{-3}.

Pyrolysis of GAP. The spectra of GAP films that were subjected to pulsed CO$_2$ laser pyrolysis at 2 J/cm^2 are illustrated in Figure 2b. A new broad band around 1660 cm^{-1} and a small band around 2032 cm^{-1} are formed after pyrolysis. We found that varying the laser fluence does not have any significant effect on the shape or position of the new bands, but simply changes the magnitude of the product absorptions.

The spectra of thin film residues formed by heating GAP to 170 °C for several minutes is shown in Figure 2c. The spectrum bears a strong resemblance to the spectrum of GAP subjected to CO$_2$ laser pyrolysis (Figure 2b) and to the spectrum of GAP subjected to UV photolysis followed by warming to room temperature for several hours (Figure 2a). The gas evolved during the 170 °C pyrolysis period was collected and found to be essentially infrared-inactive, except for a trace of CO.

Pyrolysis and Photolysis of PGN. Infrared spectra of PGN obtained before and after pulsed CO$_2$ laser pyrolysis at a fluence of about 2 J/cm^2 are shown in Figure 3a,b. Reaction product bands were observed at 1723 and 1498 cm^{-1} (CH$_2$O), 1862 (mainly NO$_2$ dimer), 1595 (N$_2$O$_3$), and 1302 cm^{-1} (NO$_2$ dimer and N$_2$O$_3$). A shoulder observed at 1744 cm^{-1} exists in the reference spectra of (NO)$_2$ and (NO$_2$)$_2$. This band persists to relatively high temperatures during the warm-up cycle, suggesting that it is mainly attributable to (NO$_2$)$_2$. In addition, small bands were observed at 2341 cm^{-1} (CO$_2$); 2133 cm^{-1} (CO); 2282 and 2276 cm^{-1} (HNCO); 2257 and 2247 cm^{-1} (HOCN); and 2236 cm^{-1} (N$_2$O). The product band observed at 1731 cm^{-1} belongs to a nonvolatile product because it persists after warming to room temperature. The band observed at 1567 cm^{-1} cannot be definitively assigned, though aliphatic nitro and nitroso compounds typically have strong absorption bands near this position.

Pyrolysis experiments carried out at 17 and 77 K exhibit similar product absorption spectra except for smaller amounts of CO that are observed at the higher temperature, due to the volatility of this product.

Figure 3c shows the gaseous products from heated PGN at 160 °C in an ordinary thermal decomposition experiment. The evolved gas was deposited onto an infrared window at 17 K. In addition to the major products CH$_2$O, NO, NO$_2$, and CO$_2$, (which were observed in the laser pyrolysis experiment), we

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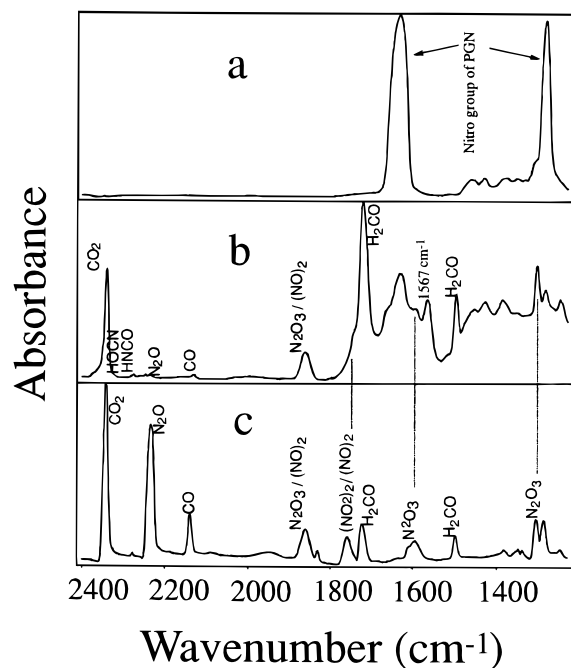*J. Phys. Chem. B, Vol. 101, No. 12, 1997* **2129**

Figure 3. Infrared spectrum of a PGN sample (a) prior to and (b) following CO_2 laser pyrolysis at 17 K. Spectrum c is a film produced by collecting the vapor evolved from a sample of PGN heated to 160 °C and condensing it onto an infrared window at 17 K in vacuum.

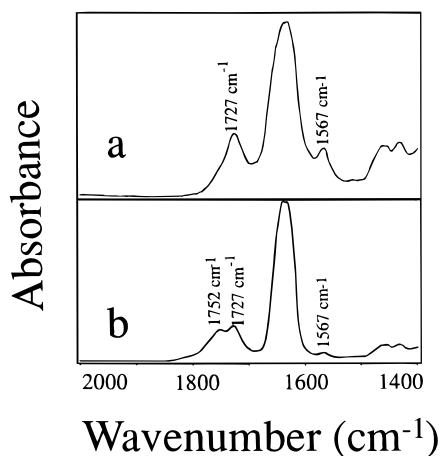**Figure 4.** (a) Partial infrared spectrum of a PGN sample that was pyrolyzed with a CO_2 laser and subsequently warmed to room temperature. (b) Residue of a PGN film that subjected to ordinary thermal pyrolysis at 160 °C.

see a significant enhancement in the intensity of bands attributed to CO and N_2O.

Thermal decomposition of PGN at higher temperature produces gaseous products CH_2O, NO_2, NO, N_2O, CO, CO_2, HCN, HONO, CH_4, and H_2O, which were detected both in the gas phase and in the low-temperature condensed phase. Explosive thermal decomposition occurs in samples of PGN, but requires somewhat higher temperatures than GAP.

In addition to the gas phase products, two bands at 1730 and 1567 cm^{-1} were observed after warming laser-pyrolyzed samples to room temperature (Figure 4a). Similar bands were observed in the residue of PGN heated to 160 °C (Figure 4b).

UV laser photolysis of PGN at 266 nm results in the spectra illustrated in Figure 5b. Compared with pyrolysis, the main difference is the much smaller amounts of H_2CO (1499 cm^{-1}) and NO (1862 cm^{-1}) produced in the photolysis experiments. A thermal annealing experiment showed that the 1862 cm^{-1} band belongs to a volatile compound and is therefore more likely
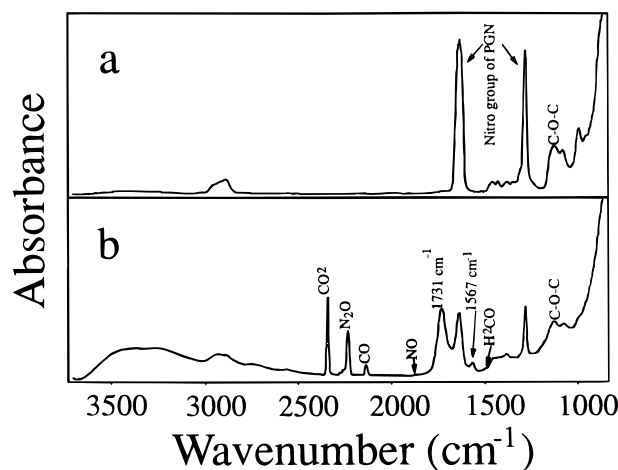

Figure 5. Infrared spectra of a PGN sample (a) prior to and (b) following 266 nm laser photolysis at 77 K.

assigned as NO in this spectrum rather than $(NO_2)_2$. The major products, CO_2, CO, and N_2O, were produced in relative amounts 1.0/1.27/1.57, after correcting for differences in infrared absorption band intensities. An excellent correlation was also found between the decrease in intensity of the PGN nitro group band and the increase of the condensed phase product band at 1731 cm^{-1}. A second condensed phase product band at 1567 cm^{-1} was also observed. A band near 1200 cm^{-1} associated with C−O−C vibrations of the polymer backbone is essentially unchanged during the photolysis period. The C−H stretching bands around 2900 cm^{-1} were decreased after photolysis, and a new broad OH band around 3200−3400 cm^{-1} appeared. During warming to room temperature, the bands at 1730 and 1567 cm^{-1} decreased about 20−40%. The C−O−C band and OH band also decreased after warming up.

The quantum yield for 266 nm laser photolysis was measured, using the technique described above, to be 1×10^{-3}.

UV Laser Photolysis of Nitromethane. To aid the interpretation of some of the experimental results with PGN, we found it necessary to investigate the UV laser photolysis of nitromethane isolated in a 17 K argon matrix at relative concentration of 1/1200. The products were found to be CH_2O, HNO, NO, CO, CO_2, HNCO, nitrosomethanol, and a small amount of N_2O, in agreement with previously published results.[17,18] The most important new result in our experiment is that, upon warming to 40 K, the argon matrix is evaporated and changes in the product band intensities were recorded. The band corresponding to HNO disappears completely, and HNCO is diminished. At the same time, the band due to N_2O is greatly enhanced.

Thermally Activated and Photolytic Oxidation of Formaldehyde. Two experiments were carried out to determine the thermal reaction products of CH_2O with NO and NO_2. Equal amounts of CH_2O and NO or NO_2 were mixed in a sealed glass tube, one end of which was immersed in oil bath at 160 °C. After 30 min, the gaseous contents of the tube were deposited onto an infrared window at 17 K. The principal products of the CH_2O + NO reaction are N_2O and CO, along with smaller amounts of CO_2. The main products of the CH_2O + NO_2 reaction are CO and NO; moderate amounts of CO_2 were also observed, along with a small yield of N_2O.

In a separate series of experiments, we prepared thin films of formaldehyde and NO by vapor deposition of the two gases directly onto a 17 K infrared window in vacuum. UV photolysis at 266 nm forms CO, N_2O, and CO_2. Similar experiments carried out by photolyzing films of formaldehyde and NO_2 at

17 K formed CO, NO, and CO_2. After extended periods of UV photolysis, N_2O also appears as a secondary product.

Discussion

UV Photolysis and Thermal Pyrolysis of GAP. Photolytic decomposition of GAP appears to take place in two distinct steps. The first is elimination of molecular nitrogen and formation of the corresponding imine,


(2)
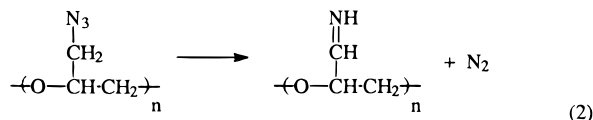
This reaction is analogous to the mechanism previously studied for simple alkyl azide compounds.[19] By analogy to the published spectra of methylenimine,[5] we may readily assign the 1652 cm^{-1} product band observed in our GAP experiments to the C=N stretching vibration of the imine product. Similarly, the 3212 cm^{-1} band is assigned to the N–H stretching vibration, and the bands at 1394 and 1224 cm^{-1} belong to NH and/or CH deformation modes.

The second stage of reaction occurs after warming to room temperature. The imine bands disappear, and the sample becomes highly light scattering. This behavior is consistent with cross-linking of the imine functional groups to form a higher molecular weight polymer. The cross-linking reaction most likely involves reaction of two imine groups with each other, rather than imine with azide. This is supported by the observation that during the room-temperature reaction there is little change in the intensity of the remaining azide band at 2103 cm^{-1}.

It is important to note that essentially all of the chemistry that occurs in the GAP reactions involves only the azide functional groups. Infrared bands associated with vibrational modes of the polymer backbone are nearly unaffected by the photolysis reaction. Moreover, the unfunctionalized poly-(propylene glycol) polymer was completely unaffected by UV laser photolysis at 266 nm.

The pyrolysis experiments (infrared laser and ordinary thermal pyrolysis) give results that are substantially similar to the UV photolysis experiments, except that the intermediate imine bands are not observed. The evolved gas from the thermal pyrolysis experiment is essentially infrared-inactive, consistent with elimination of N_2. Figure 2 demonstrates the similarity of the product spectra obtained in the two pyrolysis experiments and the UV photolysis experiment after warming. The similarity of the broad band near 1660 cm^{-1} in all three experiments is particularly significant.

Thermal Pyrolysis of PGN. Interpretation of the PGN pyrolysis experiments is straightforward. Like GAP, the reaction of PGN is centered at the nitrate ester functional groups. The observed products in these experiments are NO_2 and CH_2O, leading us to conclude that the initial step in the photolytic reaction is

(3)
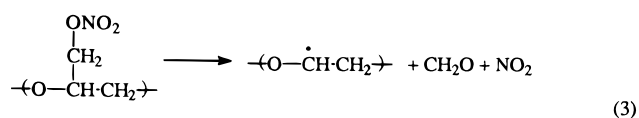
This is consistent with the conclusions of Oxley *et al.*, who studied the thermal pyrolysis of a series of nitrate ester compounds.[6] According to them, the elimination of NO_2 and CH_2O is not concerted, although we have been unable to cleanly separate the two sequential reaction steps in our experiments.

Subsequent reaction of CH_2O with NO_2 forms CO, NO, CO_2, and N_2O, in agreement with the supplementary formaldehyde oxidation experiments that were carried out in this study. It is likely that H_2O is a reaction product in this scheme; however, contamination of all samples by atmospheric water makes it difficult to isolate and quantify this. Other side reactions produce minor amounts of HNCO and possibly HOCN.

We observed a product band at 1731 cm^{-1} that is consistent with formation of a polymeric carbonyl functional group, leading us to speculate that the backbone of the polymer begins to depolymerize according to

(4)
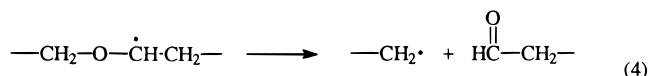
Chen and Brill had previously reported a similar band, which they attributed to formic acid decomposition product.[7,8] However, the involatile nature of the band in our experiments leads us to favor an assignment as a polymeric aldehyde. Some of the polymeric radicals in (4) may react with NO or NO_2 to form nitro and nitroso functional groups along the polymer backbone, as evidenced by the observed nonvolatile product band at 1567 cm^{-1}, which is consistent with this type of assignment.
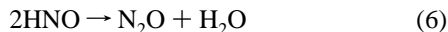
In the supplementary formaldehyde oxidation experiments, the amount of CO_2 produced was always less than CO. The thermal pyrolysis experiment on PGN also bears this out, but the pulsed infrared laser pyrolysis experiment produced greatly enhanced amounts of CO_2. It is possible that the higher temperature environment associated with the laser pyrolysis experiment causes the branching ratio for the NO_2 + CH_2O reaction to favor the CO_2 product channel. The other obvious difference between the thermal and laser pyrolysis experiments is the formation of N_2O in the former. This product is presumed to arise from CH_2O + NO_2 reactions (as shown by the supplementary formaldehyde oxidation experiments), but the short time scale of the laser pyrolysis experiment ($\sim$1 ms) precludes the formation of significant amounts of N_2O because products from thermolysis of at least two different functional groups are required to form it.

UV Laser Photolysis of PGN. The most obvious difference between the pyrolysis and photolysis experiments on PGN is that the former produces large quantities of NO_2, whereas the latter does not. Instead, we observed production of small amounts of NO and a relatively large amount of N_2O. Therefore, it is likely that in this case the photolytic reaction occurs by a different mechanism than the pyrolysis reaction. One mechanism consistent with our observations involves initial elimination of CH_2O and NO (or HNO) with formation of the corresponding polymeric carbonyl compound:

(5a)

(5b)
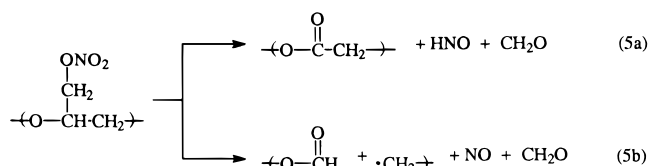
Again, reaction of the polymeric radicals in (5b) with NO or NO_2 can easily afford the observed product band at 1567 cm^{-1}, which is associated with nonvolatile nitro or nitroso products.

The N_2O, CO, and CO_2 products are presumed to arise from reaction of NO with CH_2O, consistent with our supplementary formaldehyde oxidation experiments. Of these, the N_2O product clearly arises from reactions involving at least two of the nitrate ester functional groups, e.g.

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$$2HNO \rightarrow N_2O + H_2O \qquad (6)$$

In our PGN experiments we did not detect HNO directly. However, the UV photolysis experiments that we carried out on matrix-isolated nitromethane provide indirect evidence for the participation of this reaction in our study. When isolated in an argon matrix, we observe the formation of HNO as a photolysis product. However, upon warming the argon vaporizes and allows HNO molecules to react with each other, forming N_2O.

Finally, we note that the C−O−C backbone vibrational modes of the PGN polymer are not strongly affected by the UV photolysis reaction. This suggests that depolymerization of the C−O bond in the polymer backbone is evidently not extensive.

Conclusions

UV laser photolysis and thermal pyrolysis of GAP appear to follow the same general mechanism. This begins with elimination of molecular nitrogen from the azide functional groups and rearrangement to a polymeric imine. Subsequent cross-linking of the imine groups results in a higher molecular weight polymer. For PGN, the UV laser photolysis proceeds by elimination of NO and CH_2O, followed by reactions of these species to generate several other reaction products. In contrast, pyrolysis begins with elimination of NO_2 and CH_2O, which is followed by similar side reactions that oxidize the formaldehyde to CO and CO_2. In both compounds, the reactions begin with and are centered around the azide or nitrate ester functional groups. Aside from formation of polymeric carbonyl compounds and small amounts of nonvolatile nitro and nitroso polymers, the backbone of the polymer appears to be largely inert to application of moderate heat or light stimuli.

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