Infrared and Mass Spectrometry Studies of the Thermal Decomposition of a Nitro-Aromatic Polymer

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ABSTRACT: The thermal decomposition reactions of a novel nitro-aromatic polymer were investigated. Infrared spectroscopy was used to detect chemical structure changes that occurred in the solid material when it was heated. Mass spectrometry was employed to identify volatile products. The polymer decomposition mechanisms involved reactions between nitro groups and nearby methyl or methylene functionalities and primarily resulted in the formation of nitrogen monoxide gas and hydroxyl and carbonyl groups in the solid residue. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 351–357, 2005

Key words: infrared spectroscopy; mass spectrometry; solid-state structure; thermal properties

INTRODUCTION

Energetic materials are substances that release significant amounts of energy and usually yield large amounts of gaseous products when they are heated.[1–3] Energetic materials can be classified as either explosives or propellants. Explosives generate a destructive pressure pulse when detonated, whereas propellants produce gaseous products at a relatively constant rate. Energetic materials consist of fuel and oxidant components. Fuel and oxidant functionalities can be combined within the structure of a single molecule or can be present as different materials that are mixed. Energetic materials intended for specific uses are often shaped for maximum effect. Energetic mixture components are held in a particular geometric form with polymer binders. Polymer binders can be inert or active. Inert polymer binders, such as polyurethanes, do not contribute to combustion exothermicity.[1] Active polymer binders add to the energy output of energetic materials as a result of thermal decomposition reactions that are characteristic of the polymer. Nitrocellulose and polyazides are active polymer binders that are widely employed in energetic material formulations. Nitrate esters in nitrocellulose decompose to yield NO_2, which subsequently oxidizes fuel by exothermic reactions. Azide polymers yield N_2 and release large amounts of heat when $—N_3$ functionalities thermally decompose.

Ideal candidates for new energetic materials should provide large amounts of energy and high gas yields but should be stable until ignited or detonated. In addition, these materials should be in a form that is easy to handle and transport. A unique energetic polymer was synthesized by Dinges[4] during attempts to make materials containing nitrated aromatic rings connected by strained linkages. Poly(2,5-dimethyl-3,6-dinitro-*p*-xylylene) (**1**) contains two nitro groups, two methyl groups, and one methylene group in each aromatic ring repeat unit:

1
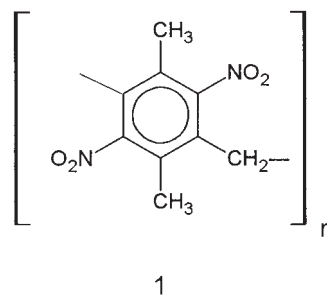
An analysis of **1** by differential scanning calorimetry (DSC) revealed that it had potential for use as an active polymer binder because it released 2.09 kJ/g when it was heated at a rate of 10°C/min in helium.[4] For comparison, 2,4,6-trinitrotoluene (TNT) produced 1.56 kJ/g in the same instrument when it was heated under identical conditions.

The thermal analysis methods previously used to study **1** provided only bulk property information (e.g., heat loss and gain and mass loss). This information provides no insight into the chemical reactions that take place during thermal decomposition. In contrast, infrared spectroscopy and mass spectrometry can be used to obtain information about the chemical structure changes that the polymer undergoes when it is

heated. Infrared spectroscopy has been used extensively to characterize the volatile products derived from energetic materials[5] but has not often been used to study changes in the solid state during decomposition. Mass spectrometry is routinely employed to detect and identify thermally generated volatile products. In this article, the chemical reactions that are responsible for the heat generation and weight loss that are observed when **1** is heated in an inert environment are identified on the basis of the results of a temperature-dependent infrared analysis of the solid residue and mass spectrometry characterization of volatile reaction products.

EXPERIMENTAL

Apparatus

Variable-temperature diffuse reflectance infrared Fourier transform spectroscopy measurements were made with a Mattson Instruments, Inc. (Madison, WI), Sirus 100 Fourier transform infrared spectrophotometer and a modified Harrick Scientific, Inc. (Ossining, NY), HVC–DRP environmental chamber.[6] Electrical power to the sample chamber heater coils was adjusted and maintained with an Omega, Inc. (Stamford, CT), CN5800 temperature controller. The temperature controller could be programmed to obtain desired sample heating rates, and measured temperatures could be read by the computer, which was also used to operate the infrared instrument. During data acquisition, a computer stored infrared interferograms as well as the temperatures measured before and after each interferogram was obtained. The sample temperature for each spectral measurement was defined as the average of the before and after temperature measurements. The samples were heated from 50 to 550°C at various heating rates. Signal averaging was used to improve the quality of the acquired spectra. Thirty-two scans were averaged for 5 and 10°C/min heating rates. One hundred scans were averaged for the 2.5°C/min heating rate. Two hundred sixty scans were averaged for the 1°C/min heating rate. Data acquisition resulted in 250 spectra for the 10°C/min heating rate and 500 spectra for the other heating rates. The infrared spectrophotometer used in this study was a single-beam instrument. As a result, the sample (polymer) and background (no polymer) measurements were made separately. After the sample interferogram measurements were completed, a mirror was used to divert the infrared beam so that it bypassed the sample chamber. After the sample chamber cooled back to 50°C, background interferograms were acquired under the same conditions that were used to measure the sample spectra. Apparent absorbance spectra were calculated by the division of each sample single-beam spectrum by its corresponding background single-beam spectrum and the negative log of the result. All infrared spectra were measured at an

8-cm^{-1} optical resolution. Mass spectrometry thermal analysis was accomplished via the heating of the samples in a tube furnace interfaced to a Hewlett–Packard (Palo Alto, CA) 5985 quadrupole mass spectrometer. The details of this apparatus and illustrations of its use for reaction kinetic studies based on the detection of volatile decomposition products have been published elsewhere.[7] DSC and thermogravimetric analysis (TGA) were conducted with a Dupont (Wilmington, DE) model 910 differential scanning calorimeter and a model 951 thermogravimetric analyzer.

Methods

The polymer was too absorbing in the infrared spectral region to be used directly. It was therefore mixed with silver powder to dilute it and reduce its absorbance. The sample used for these studies contained approximately 7% **1** and 93% silver powder by weight. Approximately 25-mg samples were weighed on an analytical balance and placed into the sample holder for each analysis. The sample chamber was purged with N_2 gas at a rate of 25 mL/min to eliminate oxygen from the reaction atmosphere. The temperature on the exterior surface of the sample chamber was held constant by flowing chilled water maintained at 18°C through a cooling jacket. This was done to avoid heating the infrared spectrophotometer optics during sample temperature ramps. Neat polymer samples weighing about 20 mg were used for mass spectrometry thermal analyses. The tube furnace interfaced to the mass spectrometer was purged with helium at a rate of 25 mL/min to eliminate oxygen from the reaction atmosphere. The same heating rates employed for infrared studies were used for mass spectrometry measurements. Neat polymer samples were heated at 10°C/min in 50 mL/min helium for DSC and TGA measurements.

RESULTS

DSC and TGA results from the thermal analysis of **1** are shown in Figure 1. TGA revealed that most of the polymer mass loss occurred between 300 and 375°C. Approximately 30% of the polymer mass was lost by 375°C, which was close to the stoichiometric NO content of the polymer (28.8%). The DSC trace showed that thermal decomposition during the 30% mass loss was significantly exothermic. Reaction exothermicity consisted of overlapping contributions with maxima near 315 and 350°C. Figure 2 shows the diffuse reflectance infrared spectrum of **1** obtained before thermal decomposition. The infrared spectrum in Figure 2 is nearly identical to one that was measured shortly after the polymer was first synthesized.[4] This suggests that little if any chemical structure change took place during the almost 5 years between the time when the
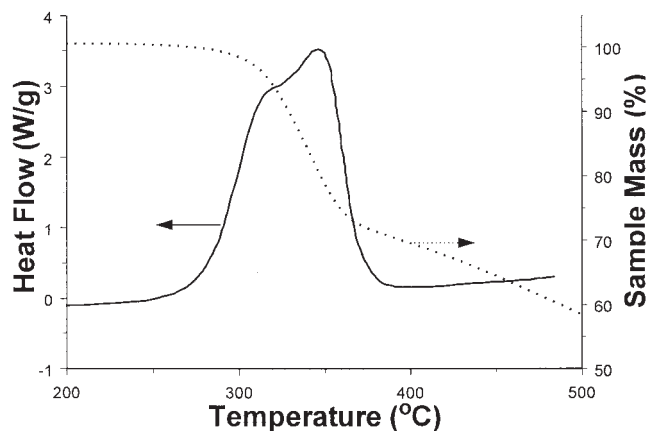
Figure 1 (—) DSC and (· · ·) TGA curves obtained during the decomposition of the nitro-aromatic polymer.

Figure 3 Diffuse reflectance infrared spectrum of the nitro-aromatic polymer at 275°C.

polymer was first made and the start of these experiments. The strong absorbance bands in the spectrum could be attributed to the polymer functional groups.[8,9] The C—H stretching vibrations between 2900 and 3000 cm^{-1} were due to overlapping methyl and methylene group absorbances by the polymer. The most intense infrared absorptions at 1540 and 1370 cm^{-1} corresponded to the polymer nitro groups. The absorbance bands below 1000 cm^{-1} were caused by aromatic ring vibrations. The smaller absorbance bands between 1000 and 1600 cm^{-1} were due to C—H bending vibrations and various aromatic ring motions. The O—H and C=O stretching vibration bands and the C—H stretching vibration near 2750 cm^{-1} (characteristic of an aldehyde functional group) labeled in Figure 2 were unexpected and could not be explained by the assumed polymer structure. The presence of these infrared bands indicated either that there were minor impurities mixed with the polymer or that the polymer had been partially oxidized during the synthesis and purification procedures.
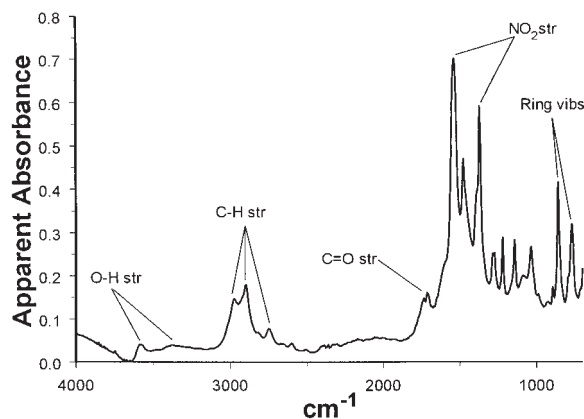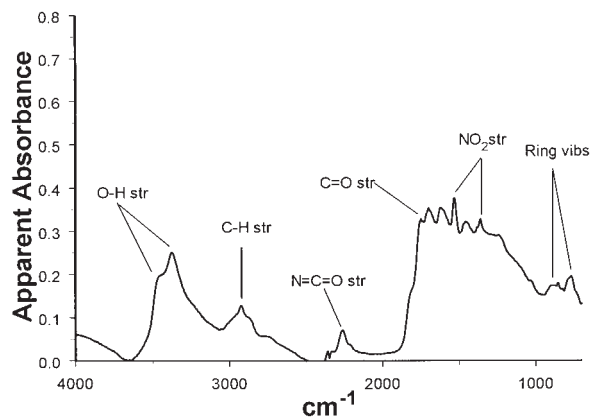

Figure 2 Diffuse reflectance infrared spectrum of the nitro-aromatic polymer at 50°C.

Figure 3 shows the infrared spectrum obtained after the polymer was heated to 275°C under nitrogen. The spectrum in Figure 3 is substantially different from the one in Figure 2 because of the structural changes that occurred in the polymer when it decomposed. A close inspection of Figure 3 reveals two strong overlapping O—H stretching vibration bands between 3400 and 3500 cm^{-1} and two strong C=O stretching vibration bands between 1700 and 1750 cm^{-1}. The nitro group and aromatic ring absorption bands are still present in Figure 3 but are greatly reduced in intensity in comparison with Figure 2. The C—H stretching vibration bands are still present, but the positions of these bands and the overall shape of the absorptions are much different from those shown in Figure 2. A band near 2270 cm^{-1} appears in Figure 3 but not in Figure 2. This band is most likely due to the —N=C=O stretching vibration.[8] The fact that this band is absent in Figure 2 confirms that the —N=C=O functional group was formed during the thermal decomposition of the polymer.

Infrared spectra acquired during the heating of the polymer provided information regarding the changes in its structure that occurred when it decomposed. Figure 4 shows the 2700–3600-cm^{-1} region of the 50°C spectrum and spectra obtained between 220 and 280°C. No significant changes in the spectral features were observed between 50 and 200°C. The O—H stretching vibration band (near 3600 cm^{-1}) in the 50°C spectrum is much smaller than those in the spectra obtained at higher temperatures. Two new O—H stretching vibration absorbance bands appear in the 220–280°C spectra. The absorbance band near 3400 cm^{-1} increases in intensity without much change in the vibration frequency, whereas the band near 3500 shifts about 40 cm^{-1} to a lower frequency with increasing temperature. In the C—H stretching vibration frequency range, absorbance peaks near 2900 and 2975 cm^{-1} decrease in intensity, and a new absorbance band near 2940 cm^{-1} appears with increasing
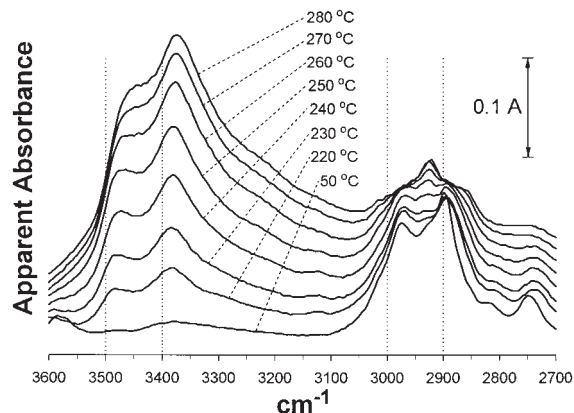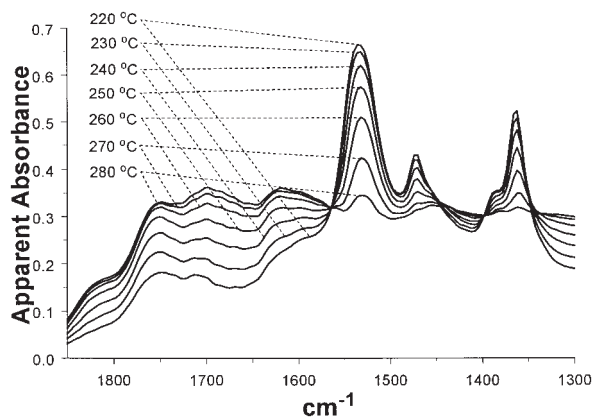
Figure 4 C—H and O—H stretching regions of infrared spectra obtained during the heating of the nitro-aromatic polymer.

Figure 6 Temperature dependence of the infrared band assigned to —N=C=O.

temperature. The 2750-cm^{-1} band, assigned to the C—H stretching vibration in —CHO, is present in the 220°C spectrum but decreases in intensity with increasing temperature. The 2700–3600-cm^{-1} spectral region changes in Figure 4 show that at least two different O—H functionalities were created, that the aldehyde functionality present at 50°C became less defined, and that the C—H stretching motions were significantly altered when the polymer was heated to 280°C.

Figure 5 shows the 1300–1850-cm^{-1} spectral region of infrared spectra obtained between 220 and 280°C. Absorbance bands assigned to the —NO$_2$ groups (1540 and 1370 cm^{-1}) decrease in intensity with increasing temperature, whereas bands near 1600, 1700, and 1750 cm^{-1} increase in intensity with increasing temperature. The 1700- and 1750-cm^{-1} absorptions are characteristic of ketone (—C=O) and aldehyde (—CHO) functionalities, respectively. The 1600-cm^{-1}

band may be due to aromatic ring vibrations for rings that have lost their —NO$_2$ groups.

Figure 6 shows the absorbance increase near 2270 cm^{-1} when the polymer was heated from 220 to 280°C. In addition to the most intense absorption near 2270 cm^{-1}, an overlapping absorbance of lesser intensity near 2210 cm^{-1} can be seen.

Mass spectrometry measurements obtained when the polymer was heated above 200°C detected ions at m/z values of 18, 28, 30, 44, and 46, which corresponded to H$_2$O, CO, NO, CO$_2$, and NO$_2$, respectively. No other ions were detected in significant abundance. The amount of NO detected was much larger than the amount of NO$_2$ detected.

DISCUSSION

Infrared spectral changes for **1** that resulted from heating could be correlated by the comparison of plots of the absorbance band intensity as a function

Figure 5 Fingerprint region of infrared spectra obtained during the heating of the nitro-aromatic polymer.

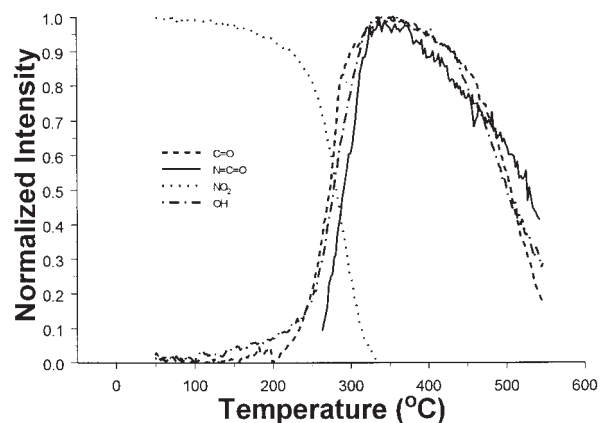**Figure 7** Functional-group-specific temperature profiles derived from diffuse reflectance spectra of the nitro-aromatic polymer.

of temperature. Functional-group-specific temperature profiles for O—H and C=O were generated by the summing of the curve-fitting peak areas of overlapping peaks that were attributed to each functional group and the plotting of this sum as a function of temperature. Temperature profiles were also generated by the plotting of the absorbance band intensities at 1540 (—NO_2) and 2270 cm^{-1} (—N=C=O) versus temperature. Figure 7 shows the resulting functional-group temperature profiles after they were normalized by the scaling of each curve so that its maximum value was unity. Infrared band changes occurred about 25°C lower than would be predicted from TGA and DSC results (Fig. 1). This shift to a lower temperature was likely due to the increased thermal conductivity of the polymer/Ag samples employed for infrared analysis in comparison with that of the neat polymer, which was used for the TGA and DSC measurements. Figure 7 shows a clear correlation between the loss of —NO_2 groups and the formation of O—H and

C=O functionalities. The O—H and C=O temperature profiles have similar shapes. Both curves show slight decreases above 350°C followed by more dramatic decreases above 475°C. Over the same temperature range, mass spectra showed that H_2O, CO, NO, CO_2, and NO_2 gases were produced when these functional groups decomposed. The —N=C=O absorbance increase began at a higher temperature than the O—H and C=O absorbance increases and then gradually decreased above 350°C. This suggested that the O—H and C=O functionalities were primary decomposition products, whereas the —N=C=O groups were secondary products.

Thermal decomposition reactions

The formation of hydroxyl groups might be explained by the insertion of one of the —NO_2 oxygens into a C—H bond. The subsequent elimination of NO gas would yield two possible radicals:

2

3
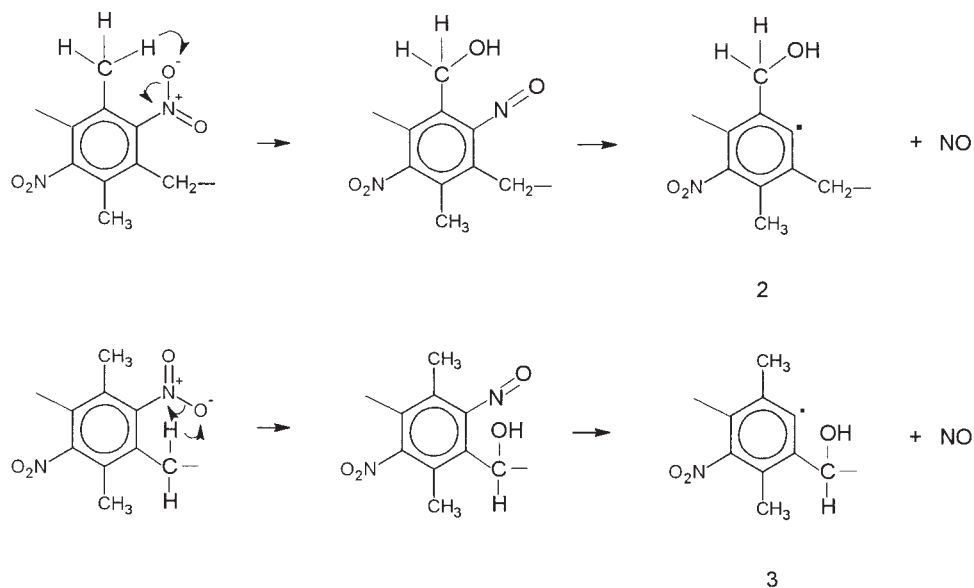
Hydrogen abstraction by these radicals (**2** and **3**) from nearby hydrocarbon portions of the polymer would result in the following two alcohol structures:

4

5
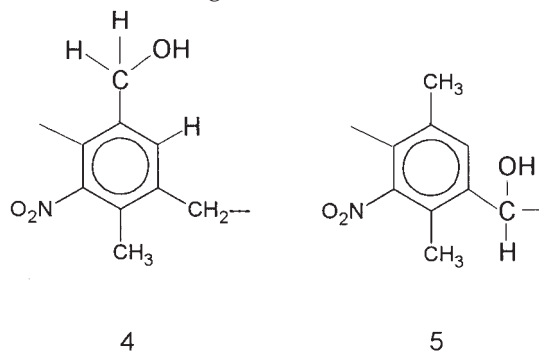
These two alcohols are responsible for the O—H stretching vibration absorbance bands that grow in intensity with increasing temperature. Structure **4** can be assigned to the absorbance band near 3400 cm^{-1}, and structure **5** is likely associated with the band near 3500 cm^{-1}. Because there are two —NO_2 groups on each aromatic ring, there should be on average two alcohol groups for each aromatic ring. The abstraction of hydrogens attached to the carbon with an alcohol group by radicals elsewhere in the polymer chain can produce —C=O functionalities. Because there are two different alcohol groups that can react with radicals, two different —C=O species can be formed:
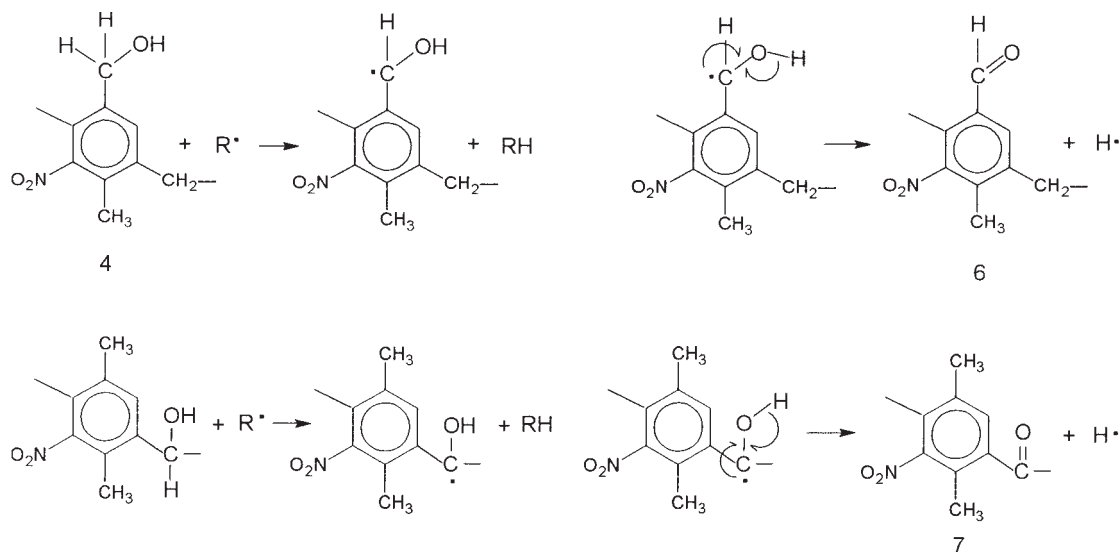
The first reaction scheme denotes the formation of an aldehyde group, whereas the second scheme shows the formation of a ketone functionality. These two species are likely responsible for the 1700- and 1750-cm^{-1} absorbance bands that increase in intensity as the sample temperature increases. The two reaction schemes shown are radical propagation reactions because one of the products of these reactions is a hydrogen radical, which can react further.

The larger redshift in the O—H stretching frequency for the 3500-cm^{-1} band, compared with that of the 3400-cm^{-1} band (Fig. 4), can be explained by differences in the opportunities that **4** and **5** have for intramolecular hydrogen bonding. Because the O—H group in **5** bridges two aromatic rings, it potentially has two opportunities for hydrogen bonding. It may form hydrogen bonds with O—H or C=O moieties formed by the oxidation of either of the two ortho methyl groups. In contrast, **4** can potentially form a single intramolecular hydrogen bond, which would be with an O—H or C=O functionality generated by the oxidation of its only ortho methylene group. Consequently, hydrogen bonds more readily form for **5** than **4**, and the 3500-cm^{-1} band exhibits a larger redshift than the 3400-cm^{-1} band.

The most likely source of —N=C=O functional groups is the reaction of NO and CO, which were detected by mass spectrometry. Previous studies of NO and CO reactions on silver surfaces have yielded infrared spectral absorbance bands near 2270 cm^{-1} (attributed to —N=C=O) that are similar to the ones shown in Figure 6.[10] Thus, it is likely that the —N=C=O functionality was adsorbed onto the silver diluent and was not present in the polymer residue.

Isoconversion activation energies

Thermal decomposition studies of the polymer were conducted at sample heating rates of 1, 2.5, 5, and 10°C/min to calculate isoconversion effective activation energies (i.e., values associated with selected conversion increments). Activation energy variations with conversion can indicate changes in the chemical reaction mechanism.[11] For infrared measurements, the sample conversion was defined as the degree to which the —NO$_2$ groups were lost. Nitro group loss was monitored by the decrease in the 1540-cm^{-1} absorbance band when the polymer was heated. The infrared-absorbance/temperature data were normalized and converted into conversions to use activation energy calculation software previously developed for mass spectrometry studies.[7] Activation energies were calculated at 5% conversion intervals from 10 to 90% conversions. Figure 8 shows that the activation energies associated with —NO$_2$ group loss from the polymer were relatively constant at just under 30 kcal/mol throughout the thermal decomposition process. Activation energy values derived from mass spectrometry measurements of the rates of NO gas formation were also relatively constant but somewhat higher than those derived from infrared measurements. The relatively constant activation energy values suggested that the rate-limiting step in the thermal decomposition mechanism did not vary with the conversion. Differences in activation energies calculated from infrared and mass spectrometry data were not unexpected because the instruments measured different aspects of the decomposition. Infrared bands decreased in intensity as soon as some of the NO$_2$ functional groups were converted into another form, and this may or may not have resulted in the formation of NO gas. On the other hand, the activation energies derived from mass spectrometry measurements reflected the kinetics of NO gas evolution, which may have occurred from intermediate structures that did not contain the original NO$_2$ group. Figure 8 also shows that the error in the infrared calculations was
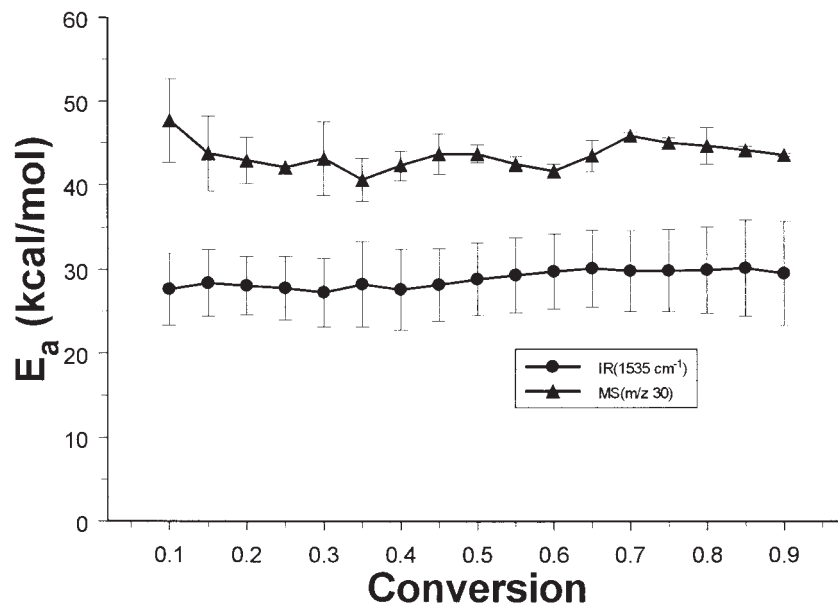
Figure 8 Isoconversion effective activation energy (E_a) values derived from mass spectrometry (MS) and diffuse reflectance infrared (IR) measurements.

greater than that for the mass spectrometry calculations. This may reflect differences in the sensitivities of the two analysis methods (i.e., infrared spectroscopy is inherently less sensitive than mass spectrometry) or may indicate that some infrared instrument parameter was varying randomly during the measurements.

CONCLUSIONS

Decomposition reactions involving NO formation are dominant processes for this nitro-aromatic polymer. Differences in the amount of energy released by the polymer and TNT might be explained by the fact that TNT does not contain enough methyl groups to react with its three nitro groups, whereas, on average, there are three alkyl groups (two methyl and one methylene) and only two nitro groups on each polymer aromatic ring. In the absence of oxygen, the energy released by the thermal decomposition of these energetic materials is determined by the oxidation of alkyl groups by oxygen derived from the nitro groups present in the material.[12] In the case of the polymer employed in this study, oxidation by aromatic nitro

groups initially led to the exothermic formation of hydroxyl functionalities, which were subsequently exothermically oxidized into carbonyl groups.

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