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EXAMINATION OF PHASE TRANSFORMATIONS AND DECOMPOSITION CHEMISTRY IN THERMALLY AGED THIN-FILM EXPLOSIVES*

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ABSTRACT

To develop predictive models for the response of weapon systems to abnormal thermal environments, such as cookoff, an improved understanding of temperature-dependent thermophysical phenomena (such as phase transformations) and decomposition chemistry in totally confined explosive samples is needed. It is particularly important to examine the effects of maintaining intimate contact between the decomposition products and the remaining condensed-phase explosive during slow reaction at elevated temperatures since confinement of the decomposition products may significantly affect thermophysical phenomena and decomposition reaction rates.

The purpose of this work has been to examine experimentally the effects on condensed-phase chemistry which result when decomposition products remain in intimate contact with the reacting explosive during isothermal aging experiments at temperatures below those of the DTA exotherm for the explosive. To provide confinement, minimize vapor space, and permit condensed-phase chemical analysis, experiments were done using thin-film samples of the explosive, which were pressed and sealed between two infrared-transmitting windows, so that condensed-phase chemistry could be monitored using infrared spectroscopy. Experiments were done with NC, HMX, HMX-NC composite, and RDX samples. Results from the experiments with NC showed that for some decomposition mechanisms, the reaction rates for confined samples compared favorably with published reaction rates from unconfined samples. However, the results also demonstrated that for other mechanisms, the reaction rates were significantly affected by confinement of the decomposition products. The experiments with HMX and RDX indicated that some decomposition occurred at temperatures well below the temperatures of the respective DTA exotherms, and the experiments with HMX-NC composite samples showed some interaction between NC and HMX at temperatures as low as 150° C.

INTRODUCTION

To develop predictive models for the response of weapon systems to abnormal thermal environments, an improved understanding of temperature-dependent thermophysical phenomena (such as phase transformations) and decomposition chemistry in totally confined explosive samples is needed. It is particularly important to examine the effects of maintaining intimate contact between the decomposition products and the remaining condensed-phase explosive during slow reaction at elevated temperatures since confinement of the decomposition products may significantly affect thermophysical phenomena and decomposition reaction rates.

The accumulation of decomposition products in the condensed phase can affect several physical phenomena that influence weapon system response in an abnormal thermal environment. The nature of these effects

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will depend on the degree of miscibility between the decomposition products and the remaining explosive. In the case of low miscibility, the separation of decomposition products into separate phases, possibly accompanied by fracturing of solid phases, can result in an extremely heterogeneous, reacting system. In the case of high miscibility, the dissolution of decomposition products in the explosive can result in: (1) volume changes leading to void or bubble formation and (2) lowering of the temperatures at which phase transitions occur, either solid-liquid or solid-solid, which can cause additional volume as well as enthalpy changes. Such physical changes can increase the sensitivity of explosives to impact as well as increase the severity of the thermal response of the material.

The accumulation of decomposition products also can have a substantial effect on the overall rate of reaction during decomposition. The overall rate can be influenced by the reaction of a particular decomposition product with another and by reaction of decomposition products with the remaining explosive, in which case, autocatalysis mechanisms are particularly important. Also, a phase transition induced by dissolution of decomposition products can result in increased reaction rates. However, studying these condensed-phase reactions is generally impractical using bulk materials, because of the inherent difficulties in probing condensed-phase chemistry.

The purpose of this work has been to examine experimentally the effects on condensed-phase chemistry which result when decomposition products remain in intimate contact with the reacting explosive during isothermal aging experiments at temperatures below those of the DTA exotherm for the explosive. The approach taken in this work has been to study condensed-phase chemistry using totally confined thin-film samples, which allow infrared spectroscopy to be used to determine solid-solid phase transitions, in materials such as HMX, and to examine condensed-phase chemistry in several materials. Furthermore, other physical effects such as liquefaction and bubble or void formation can be examined using optical microscopy and video photography. Experiments have been done using a variety of explosives, including NC, HMX, and RDX. Results from the experiments with NC showed that for some mechanisms, the reaction rates for confined NC samples compared favorably with published reaction rates for unconfined samples. However, the results also demonstrated that for other mechanisms, the reaction rates were significantly affected by confinement of the decomposition products. The experiments with HMX and RDX indicated some decomposition at temperatures well below the respective DTA exotherms, and the experiments with the HMX-NC composite samples showed some interaction between NC and HMX at temperatures as low as 150° C.

In the following discussion, the thin-film experimental techniques that were developed are first briefly summarized. Then, the results from experiments with NC, HMX, HMX-NC composite, and RDX samples are presented and discussed.

EXPERIMENT

The objective of the experimental work was to examine the decomposition chemistry of explosives such as NC, HMX, and RDX when intimate contact was maintained between decomposition products and the remaining explosive. The experiments required a sample configuration which provided maximum confinement of the decomposition products, involved minimum free volume around the explosive, and allowed the condensed-phase chemistry to be probed directly. This was accomplished using the configuration shown schematically in Fig. 1. Samples of a single energetic material, such as NC, HMX, and RDX, were used to study decomposition of initially pure explosives, and composite samples of materials, namely HMX and NC, were used to study the interaction between constituents in HMX-NC formulations. The NC used was 11.8 weight percent N.

To prepare samples of RDX, HMX, and NC, a thin-film, about 2 to 5 microns thick, of the explosive was deposited on an inert infrared-transmitting substrate, such as a barium fluoride or sodium chloride optical window. A second window was pressed against the surface of the explosive, and the perimeter around the film and windows sealed. Composite samples of HMX and NC were prepared similarly except that the HMX was deposited on one window and NC on the other. The HMX layer was then pressed against the NC layer, and the perimeter sealed. The sealed sample was next placed in a secondary stainless steel container that was sealed and then placed in an oven maintained at the desired reaction temperature. Typical reaction temperatures were about 130 to 170° C, and typical reaction times about 2 to 48 hours. Afterwards, the secondary container was removed from the oven and cooled in air. Cooling required about one hour.

The sample was then removed from the secondary container and placed in an infrared spectrometer for postmortem analysis.

The preparation of thin-film explosive samples has been discussed previously.[1] Briefly, the procedures for preparing samples are based on either physical vapor deposition or on deposition from solution. Physical vapor deposition provides reasonably precise control of film properties. The technique can be used with any material, such as RDX or HMX, that exerts sufficient vapor pressures at temperatures low enough to preclude decomposition of the material. However, polymeric materials such as NC do not exert sufficient vapor pressure. For these materials, the simplest alternative is deposition from solution, which may not permit as precise control of film properties. Using physical vapor deposition, good quality samples of RDX and HMX have been deposited on a variety of substrates that include tungsten, aluminum, nickel, gold, pyrex, barium fluoride, and sodium chloride. Film thicknesses have been varied between about 0.04 to 10 microns. Good quality films of NC, about 0.5 to 5 microns thick, have been prepared by evaporation of acetone solutions containing 0.1 to 1 weight percent NC. The characterization of sample films prepared using the above procedures also has been discussed previously.[1] In general, films that are uniform and well-crystallized should be chemically representative of bulk materials. To determine uniformity and crystallinity, several thin-film samples were examined by optical and scanning electron microscopy, x-ray diffraction, and transmission electron microscopy. The optical and scanning electron microscopes were used to examine film morphology and uniformity. The films exhibited some microscopic surface roughness, but overall, they appeared relatively uniform, flat, and nearly fully dense. X-ray diffraction was used to examine the crystal structure of samples having thicknesses of about 2 microns or greater. The diffraction patterns obtained from the thin-film samples agreed with published data and exhibited very narrow peaks, which indicated that the films were well-crystallized. The films were polycrystalline, but the grains appeared to be highly oriented. To determine the uniformity and crystal structure of submicron-thick films, procedures were developed to examine samples with the transmission electron microscope. The electron diffraction patterns from RDX films, 0.5 microns thick, showed that the crystal structure of the films was that of bulk RDX. The 0.5-micron films were also polycrystalline and highly oriented, with the [001] zone of most of the grains being perpendicular to the substrate plane, which is consistent with the x-ray diffraction result from thicker films. In addition to examining film uniformity and crystallinity, infrared spectra were obtained from RDX and HMX films, 2 to 5 microns thick. These spectra were in good agreement with the corresponding published spectra.

RESULTS

Results from isothermal decomposition experiments done with NC, HMX, HMX-NC-composite, and RDX samples are described below.

NC

The decomposition of NC films was studied previously by Phillips et al.[3] and Jutier et al.[5], who used infrared spectroscopy to examine decomposition mechanisms and kinetics. The principal infrared absorption frequencies for NC are shown in Table 1.

Phillips et al. examined isothermal decomposition into vacuum. Decomposition temperatures were varied between 140 and 200° C. The NC films were typically 3 microns thick. The principal decomposition mechanisms observed by Phillips et al. were scission of the O-N bond in the nitrate groups, the corresponding carbonyl formation by scission of an adjacent C-C bond, and the scission of the C-O-C bonds involving both ring and linking oxygen atoms. Scission of the O-N bond, carbonyl formation, and scission of the C-O-C bond all appeared to be first-order processes, for which Arrhenius expressions, activation energies and frequency factors were evaluated. The rate of scission of the C-O-C bond was approximately equal to the rate of scission of the O-N bond. The rate of carbonyl formation appeared to be approximately equal to or greater than the rate of O-N bond scission. The spectra reported by Phillips et al. also indicated scission of the C-H bonds. Furthermore, a broad, but weak absorption in the O-H/N-H stretching region appeared to develop slowly.

Jutier et al. conducted nonisothermal experiments using a heating rate of 0.5 °C/s. FTIR spectra were acquired between 140 and 200° C. Their results were similar to those of Phillips et al., except that

Jutier et al. claimed that the C-O-C bond involving the linking oxygen atom remained intact during their experiments.

In general, some of the reaction mechanisms implied by the IR spectra obtained during decomposition of totally confined samples would be expected to be similar to those observed by Phillips et al. and Jutier et al. during decomposition of unconfined samples. However, other mechanisms would be expected to be dissimilar. The infrared spectra obtained during decomposition of the confined samples do indicate similarities as well as differences. Figure 2 shows the spectra from 5-micron-thick NC films aged at 130 and 150° C for 16 hours. The initial spectrum prior to heating is also shown for comparison. At 130° C, some decomposition is evident. A small decrease in absorption, relative to the initial spectrum, occurred at the NO_2 stretching frequencies, indicating scission of the O-N bond. Some absorption at the C=O stretching frequency was present, indicating carbonyl formation. A small loss in absorption due to C-O-C stretching also occurred, indicating scission of the C-O-C bond, and a loss in absorption at the C-H stretching frequencies was evident, indicating some hydrogen abstraction. Some absorption also appeared to occur at 1580, 1350, and 1200 cm^{-1}. At 150° C, the changes in the absorptions, relative to the initial spectrum, at the O-N, C=O, C-O-C, and C-H stretching frequencies are much more pronounced and indicate that scission of the O-N bond, carbonyl formation, scission of the C-O-C bond, and hydrogen abstraction are substantial. The absorption in the O-H/N-H stretching region has broadened, shifted, and substantially increased, and the absorptions at about 1580, 1350, and 1200 cm^1 also have increased substantially. These effects are evident even after relatively short aging times, as shown in Fig. 3, which compares the spectra from samples aged for 2 and 16 hours at 150° C.

The decrease in the absorptions at the O-N, C-O-C, and C-H stretching frequencies and the growth of the absorption at the C=O stretching frequency are evident in the spectra from both confined and unconfined samples. The significant absorptions at the O-H/N-H stretching frequencies and the apparent absorptions at about 1580, 1350, and 1200 cm^{-1} are unique to the confined samples, and may be associated with the NC or may be due to accumulation of decomposition products.

Beer's law was assumed to examine the reaction rates associated with the spectral changes shown in Fig. 3. The results are summarized in Table 2 which shows the various changes in absorbance A at time t relative to the absorbance A_o prior to aging. In the case of carbonyl formation (C=O), the ratio $A/A*$ is shown, where $A*$ is the value of A at 16 hours.

Values of the ratio $[\ln(A/A_o)]/t$ also are shown as a function of time. The ratios for the NO_2 stretching frequencies, which indicate scission of the O-N bond, and the ratios for C-O-C stretching, which indicate scission of the C-O-C bonds, are approximately constant with time, indicating that bond scission occurs by a first-order mechanism. However, the decrease in absorption at the C-H stretching frequencies and the increase in the N-H/O-H stretching frequencies do not indicate first order mechanisms. In the case of C-H stretching, the ratio A/A_o initially decreases much faster than the ratio for O-N and C-O-C bond scission, but between 2 and 16 hours decreases much slower. In the case of O-H/N-H stretching, the broadening and shifting of the absorption probably results from multiple mechanisms involving reaction of the decomposing NC and formation of decomposition products. Furthermore, the values of $A/A*$ for C=O stretching indicate that carbonyl formation is not first-order with respect to O-N bond scission.

The results from decomposition experiments with confined samples and the results from experiments with unconfined samples are similar with respect to O-N and C-O-C bond scission. With both confined and unconfined samples, the bond scissions apparently occur by first-order processes. However, the relative rates at which scission occurs differ between confined and unconfined samples. Phillips et al. reported that with their unconfined samples, the rate of C-O-C bond scission was approximately equal to the rate of O-N bond scission. However, with the confined samples described above, the rate of C-O-C bond scission appeared to be about 40 percent greater than the rate of O-N bond scission.

The results also differ with respect to carbonyl formation. Phillips et al. reported that carbonyl formation was a first order process having rates approximately equal to, or greater (by as much as 40 percent) than the rate of O-N bond scission. However, with confined samples, carbonyl formation does not appear to be first order, and the rate of formation, between 2 and 16 hours appears slower than the rate of O-N bond scission at 150° C.

The results further differ with respect to the strong absorption which develops at the O-H/N-H stretching frequencies. Clearly the formation of O-H or N-H containing products was much more significant with confined samples.

HMX AND HMX-NC COMPOSITE

Experiments with HMX have been limited, partly due to the frequent failure of the seals around the perimeter of the samples at temperatures above 150° C. Figure 4 shows results from a 5-micron-thick HMX sample aged at 150° C for 16 hours. The initial spectrum prior to heating and the room-temperature postmortem spectrum after aging for 16 hours are both shown in the figure. A significant absorption at about 1665 cm^{-1} developed during aging and may correspond to a nitramine-to-nitrite rearrangement.

The interaction between HMX and NC was also examined at 150° C. Figure 5 shows the results from a HMX-NC composite sample aged at 150° C for 16 hours. The sample consisted of a 5-micron-thick HMX film pressed against a 0.5-micron-thick NC film. Since the ratio of HMX to NC was large, the two sharp absorptions at about 2920 and 2850 cm^{-1} were most likely due to a HMX reaction mechanism and indicate some interaction between HMX and NC, because the absorptions did not occur with HMX that was aged at the same conditions.

Since the rate of decomposition of NC is much greater than the rate of decomposition of HMX at temperatures of about 150 to 200° C, the interaction of NC decomposition products with HMX has two potential effects on the behavior of formulations involving NC and HMX: (1) accelerating the rate of decomposition of HMX and (2) lowering the temperatures of solid-solid or solid-liquid HMX phase transitions, which could, in turn, accelerate reaction rates as well as cause substantial density changes as shown in Table 3. The procedures for investigating phase transition effects are being developed. Initial work has been directed toward determining conditions necessary to prepare thin-film samples of the desired HMX phase. Samples of both β and δ HMX have been prepared, although some uncertainty exists regarding the conditions which yield each phase. In initial experiments with samples of β HMX aged at 150° C, room-temperature postmortem analyses indicated β HMX after aging and cooling. However, in experiments with samples of δ HMX, postmortem analyses indicated α HMX after aging and cooling.

RDX

Results from isothermal aging experiments with RDX have been discussed previously.[2,4] Those experiments indicated that some decomposition occurred during aging at temperatures as low as 170° C. For example, after aging for 18 hours at 170° C, a broad absorption occurred at wavelengths between about 2.5 and 3.0 microns, in the O-H/N-H stretching region, which probably indicates formation of H_2O or other OH-containing species. A broad absorption also occurred between 3.0 and 3.5 microns and may indicate partial degradation of the RDX ring, which would be consistent with a decrease in absorption that occurred at about 3.25 microns, the wavelength for C-H stretching in RDX. Another broad absorption also appeared to occur at wavelengths between about 3.75 and 4.5 microns, which suggests the formation of some nitrile compounds.

Similarly to HMX, the accumulation of RDX decomposition products can affect the rate of decomposition of the remaining RDX as well as the solid-liquid phase transition temperature. In fact, an apparent effect on phase transition was observed and reported previously by Erickson et al.[6] In that work, video photography of 10-micron-thick samples of RDX heated at about 15 °C/s showed partial liquefaction beginning at temperatures between 160 and 170° C.

SUMMARY AND CONCLUSIONS

The results from the isothermal aging experiments using thin-film samples have been encouraging. The experiments with NC demonstrated that confinement of decomposition products in intimate contact with the remaining explosive can influence decomposition reactions. Some of the mechanisms and reaction rates determined from the experiments with confined samples compared favorably with published mechanisms and reaction rates from unconfined samples. However, other mechanisms and reaction rates differed between confined and unconfined samples. These differences should currently be considered tentative, since uncertainty exists in evaluating overlapping absorbances at some frequencies, and deviations from Beer's law can occur.

Interaction between HMX and NC was observed at temperatures as low as 150° C, and some decomposition of RDX and HMX was observed at temperatures well below the respective DTA exotherms.

A disadvantage of the postmortem analyses used in the experiments described above was that the sample had to be cooled before infrared analysis. In recent work, this disadvantage has been overcome by placing the sample assembly in a heated cell which fits in the sample chamber of the infrared spectrometer. Further improvements to the experiments will include improved metal seals, which will allow experiments at higher temperatures, and the use of FTIR, which will allow frequent, real-time data acquisition while samples are at their aging temperatures, and will facilitate acquiring data at several aging temperatures and times. With these improvements, the isothermal aging experiments should provide substantial insight into the decomposition mechanisms of a variety of explosives and formulations.

ACKNOWLEDGMENTS

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TABLE I. Infrared Absorption Frequencies for NC.[5]

Frequency (cm^{-1})	Relative Intensity	Assignment
3512	weak	OH stretching
3515	weak	OH stretching
2973	medium	CH_2 asymmetric stretching
2927	medium	CH stretching
2883	medium	CH_2 symmetric stretching
1653	very strong	NO_2 asymmetric stretching
1424	weak	CH_2 bending
1375	medium	CH bending
1282	very strong	NO_2 symmetric stretching
1160	medium	asymmetric oxygen bridge stretching
1118	medium	asymmetric ring stretching
1070	very strong	C-O stretching in C1-O-C4'
1025	weak	C-O stretching
1004	medium	C-O stretching
0910	weak	C-O stretching
0840	very strong	O-NO_2 stretching
0749	medium	O-NO_2 deformation
0692	medium	O-NO_2 deformation

TABLE II. Analysis of Spectra.

Absorption	t (hr)	A/A_o	$A/A*$	$\frac{\ln(A/A_o)}{t}$	k (hr^{-1})	
					This Work	Phillips et al.[3]
NO_2 asym	0	1.0	—	—	0.11	0.10
	2	0.77	—	0.13		
	16	0.19	—	0.10		
NO_2 sym	0	1.0	—	—		
	2	0.84	—	0.09		
	16	0.21	—	0.10		
C=O	0	—	0	—	—	0.17
	2	—	0.35	—		
	16	—	1.0	—		
C-O-C	0	1.0	—	—	0.14	0.11
	2	0.77	—	0.13		
	16	0.09	—	0.15		
C-H	0	1.0	—	—	—	—
	2	0.58	—	0.27		
	16	0.32	—	0.07		
O-H/N-H	0	1.0	—	—	—	—
	2	1.48	—	—		
	16	2.78	—	—		

Table III. Density of HMX Phases.[7]

Phase	Density (g/cm^3)
β	1.903
α	1.87
γ	1.82
δ	1.78

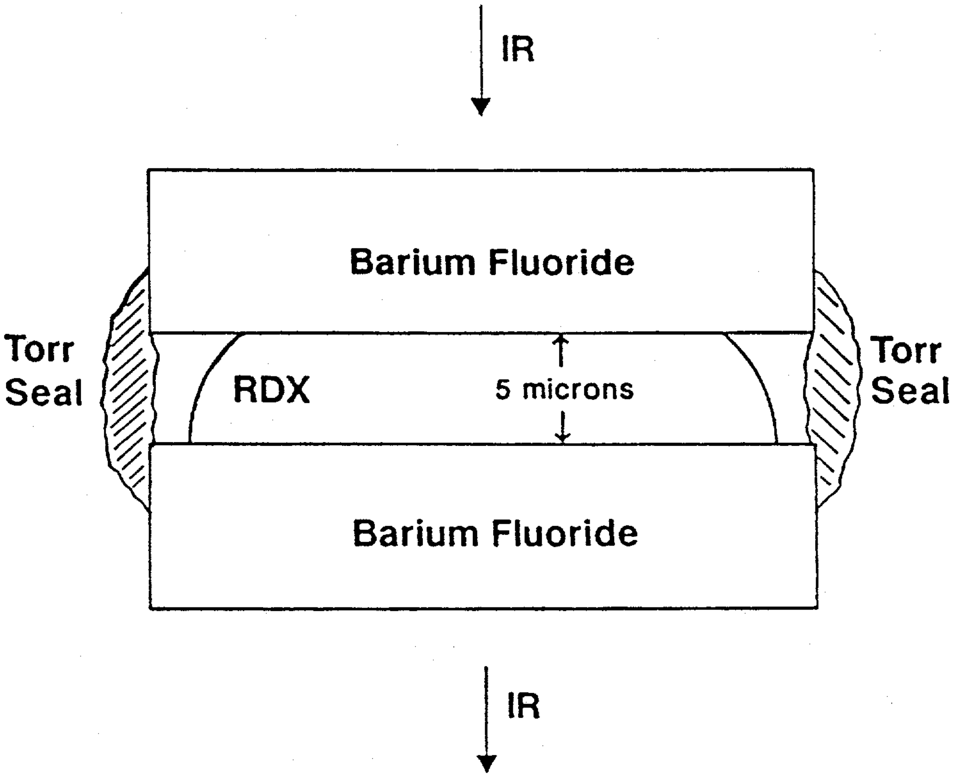

Figure 1. Sample configuration used in thermal aging experiments.

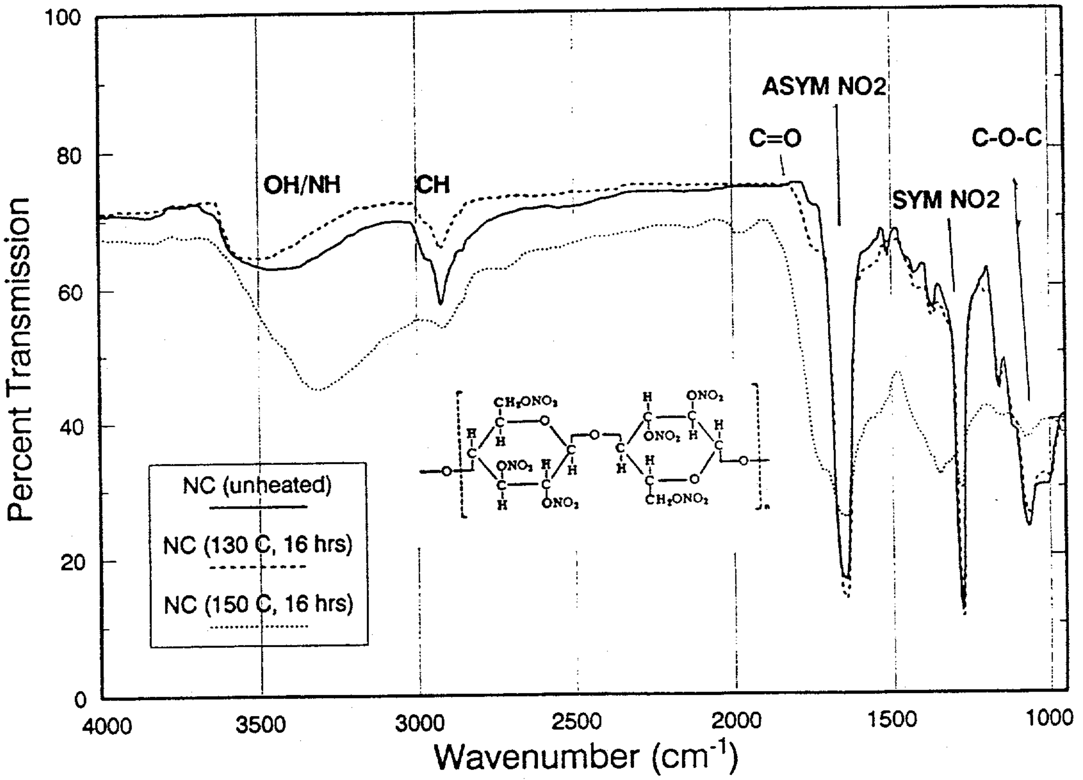

Figure 2. Infrared spectra from 5-micron-thick NC samples aged for 16 hours at 130 and 150° C.

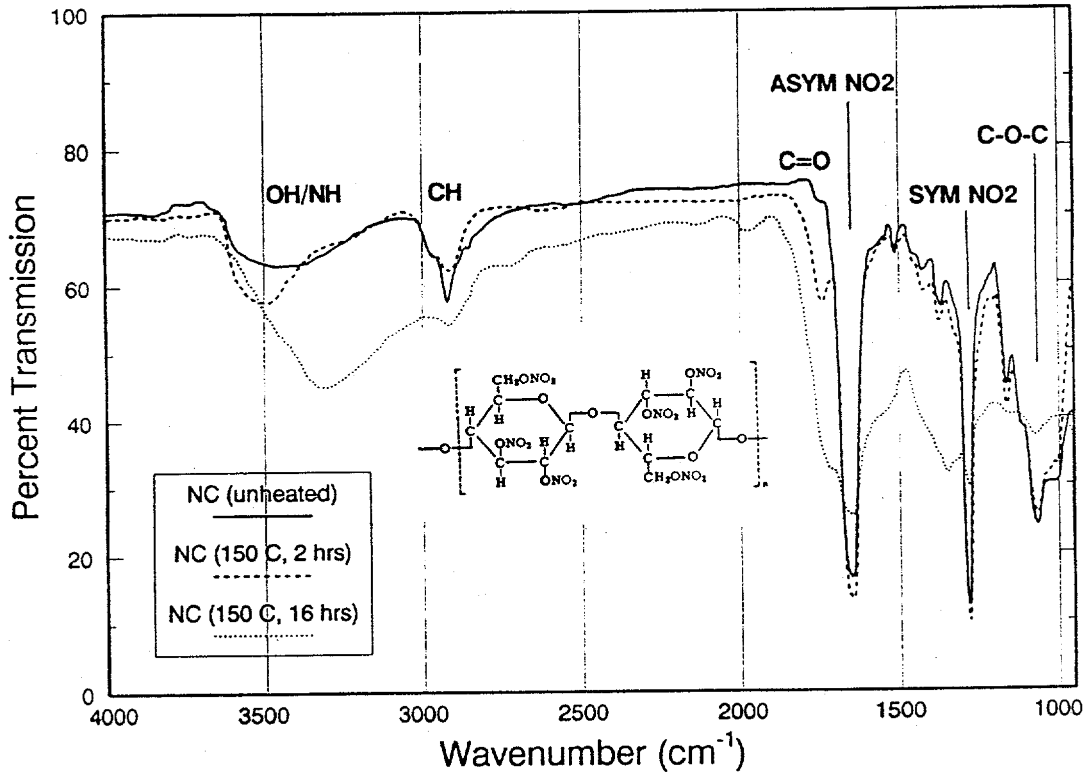

Figure 3. Infrared spectra from 5-micron-thick NC samples aged for 2 and 16 hours at 150° C.

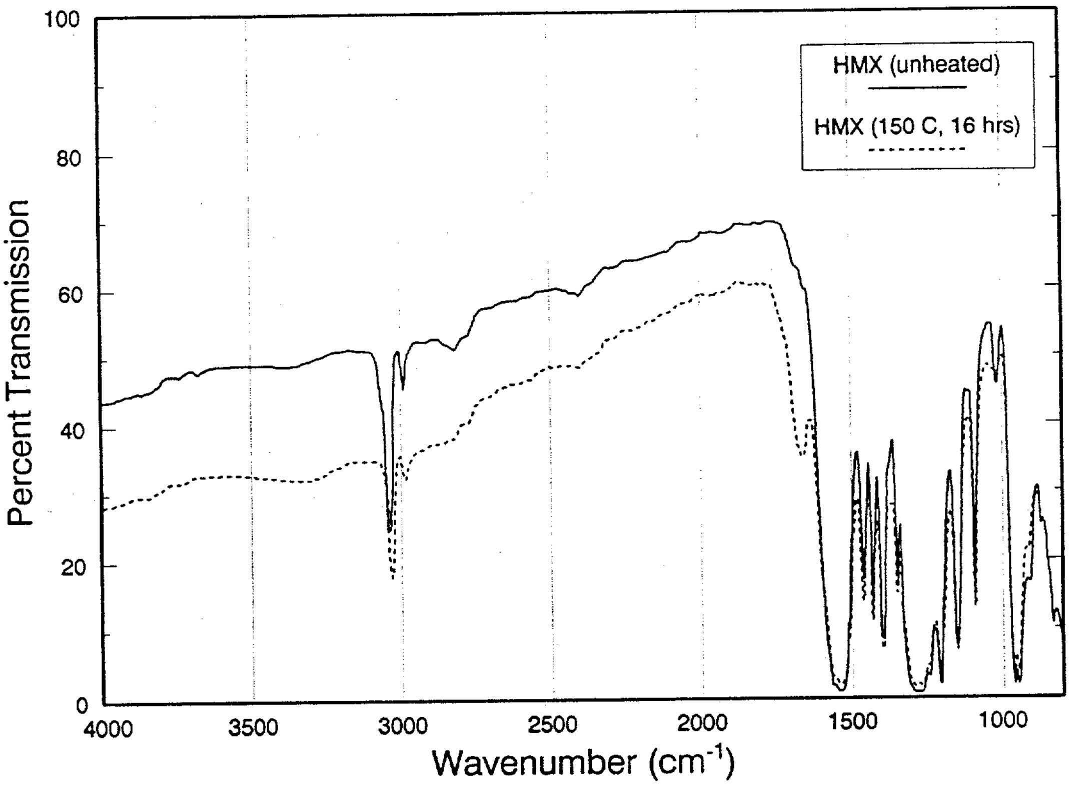

Figure 4. Infrared spectra from 5-micron-thick HMX sample aged for 16 hours at 150° C.

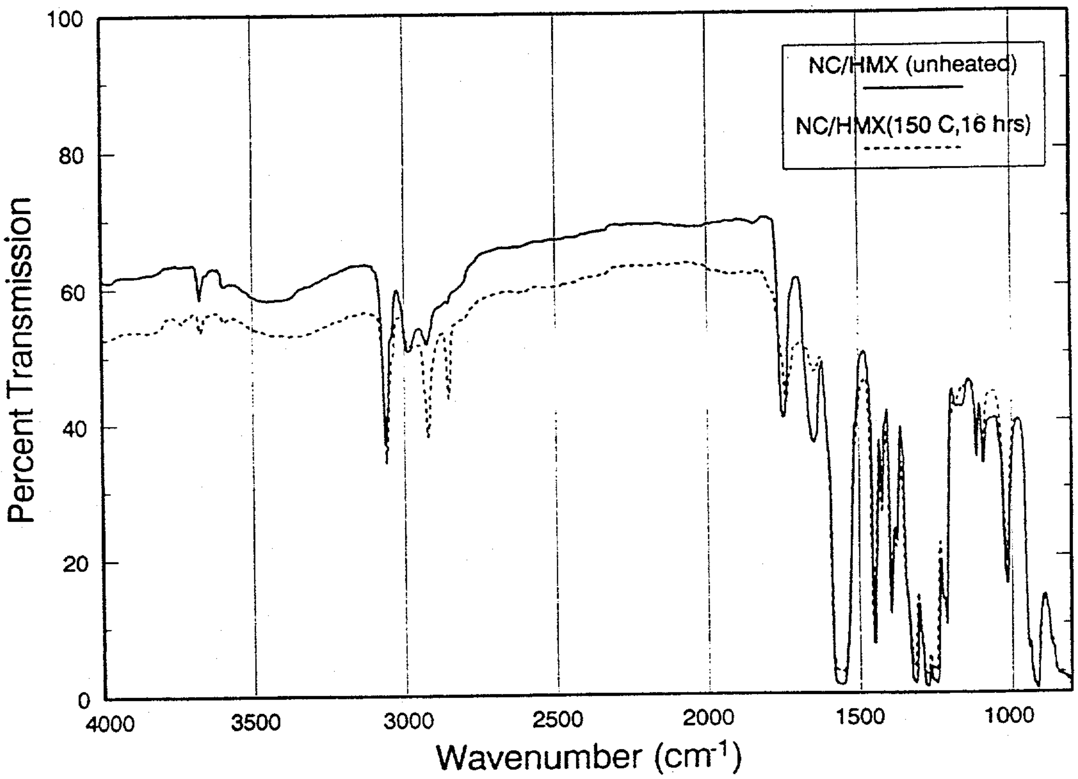

Figure 5. Infrared spectra from HMX-NC composite sample aged for 16 hours at 150° C (5-micron HMX film, 0.5-micron NC film).