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THE THERMAL DECOMPOSITION CHEMISTRY OF CL-20

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ABSTRACT

The relatively new energetic material 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazoisowurtizane (CL-20) shows significant promise as an additive to propellant formulations due to its high energy density. Characterization of the thermal stability and thermal decomposition kinetics and chemistry is undertaken to better understand performance and safety issues of this material. Experiments using the Simultaneous Thermogravimetric and Modulated Molecular Beam Mass Spectrometry (STMBMS) apparatus at Sandia/CA are used to analyze the decomposition products from heated CL-20. A quantitative analysis of the experimental data with a comparison to models and previous literature is employed to better understand the completion between NO_2 and NO loss from the decomposing material. Other results of interest include a particularly rapid decomposition observed at temperatures above 205 degrees Celsius even under conditions of low confinement. Ultimately, a thorough characterization of the thermal decomposition chemistry of CL-20 provides a foundation for understanding the complex interactions at work in multi-ingredient formulations.

INTRODUCTION

Begin the introduction here. The incorporation of novel energetic materials into active technology has seen success with CL-20, due basically to its superior performance and reasonable sensitivity. The chemical processes active in the decomposition of the compound are of interest for study of both performance and stability characteristics. There is a complex interaction between these characteristics and the exact chemical properties that evolves over time when subjected to a stimulus. Due to the variety of molecular degrees of freedom, the types of chemical processes that are active are strongly dependent upon the time-scale of the stimulus.

There has been much work done on the detonation properties and shock sensitivity of CL-20, as well as ageing and chemical interaction studies. Of course the solid state properties of the compound have received enormous attention, an interesting example is the recent work of Molt and Bartlett, et. al [4] that presented an ab-initio study of the stability of the molecule conformers in which they directly related the various molecular confirmations to the corresponding polymorph structures. In addition, there is a body of open literature on the dissociation and decomposition of the compound. There are some very useful results, such the definitive study of the basic thermal properties by Turcotte *et al.* [1] that included decomposition. There are some very interesting papers by physical and computational chemists, as well. These papers deal with the unimolecular dissociation properties of CL-20, such as the work of Guo and Bernstein and co-workers in 2007 that showed UV-photoexcitation of gas-phase CL-20 produces NO [2]. There is a relationship between the gas-phase unimolecular decomposition processes and the solid-state decomposition chemistry, and the very interesting study of Isayev *et al.* [3] in 2008 that explored this computationally in a MD simulation that addressed the ps time-domain range at kK-range temperatures.

Like much of the literature on reactive chemistry in energetic materials, there is a certain lack of clarity in regards to both the timescale and variety of the active chemistry. The current study seeks to facilitate the overall discussion by imposing attention on defining the time frame of the stimulus, measurement and chemical processes under discussion. While the individual molecular-level events that comprise a chemical decomposition process can happen extremely rapidly, what is typically measured the net effect of many. Thus, the interaction of the products with each other must be foremost in consideration. In particular, ageing and thermal decomposition processes show highly inter-reacted chemical compositions over a measurement time-frame. Previous studies of thermal properties show that CL-20 is stable up until about 200 °C. The studies on a fast time scale show that there is a competition between NO and NO_2 loss. The current study explores the overall chemistry at play in the thermal decomposition of CL-20 and also examines the role of direct NO_2 loss from the sample.

EXPERIMENTAL

The primary experimental approach employed in the current study is mass spectrometry analysis of heated samples using the instrument/technique developed at Sandia for this purpose, the Simultaneous Thermogravimetric and Modulated Molecular Beam Mass Spectrometer. This instrument has been previously described in detail [4] and only a basic account is provided here.

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The experiment consists of heating a sample while simultaneously measuring the weight loss of the sample and the mass spectrum of the vapors evolved. The chemical identity of the products is determined by comparison of the measured m/z value with the molecular weight of likely candidates. The reaction chemistry as a function of time is determined by examination of a series of mass-spectra of the heated sample. These experiments are performed under low confinement such that the gaseous reaction products do not significantly pressurize the cell.

Typical experimental heating profiles consist of isothermal temperature holds and temperature ramps, which give different decomposition results based upon the temperatures achieved and the heating rate. For the current study, we examine three isotherms and three ramps, as outlined in the Table 1. below. The heating rate and temperature strongly affect the degree of reaction in the sample.

Description	Index	Notes
isotherm @ 175 °C	008	slow decomposition
isotherm @ 185 °C	004	slow decomposition
isotherm @ 195 °C	013	fast decomposition
ramp to 240 °C	001	very fast decomposition
ramp to 400 °C	012	very fast decomposition
ramp to 500 °C	011	very fast decomposition

Table 1. Description of Heating Profile for CL-20 STMBMS Experiments

These two sets of three experiments comprise our experimental data set for this study. We measure the weight and temperature of the sample while recording mass-spectra of the vapors evolved from the sample. The data from the experiment consists of a matrix of intensities of individual *m/z* values uniquely correlated with the measurement time, mass, and temperature of the sample.

RESULTS AND DISCUSSION

The results of the study address the following topics: basic decomposition behavior (the mass loss rate as a function of temperature), overall chemical pathways (what general chemical species are observed from the sample), and the role of NO2 in the decomposition (the determination of whether NO2 is a decomposition product).

BASIC DECOMPOSITION

Upon heating, the CL-20 sample decomposes very slowly at temperatures below 180°C, but undergoes a very rapid decomposition above about 190°C. This type of behavior was observed in the study of Turcotte *et al.* [1], and is very dramatic in the current study. The temperature ramps shown in panel (a) of Fig. 1 produce the mass loss curves in panel (b). As seen in Figure 1, all the temperature ramps result in a very fast decomposition event, so fast that for a couple of these scans a “thrust event” was observed; the force of gaseous expulsion countered the weight loss. Because the temperature ramps are at different rates, the time of the rapid decomposition is different for the three scans. However, as shown in panel (c) of Fig. 1, if the mass loss is plotted as a function of temperature, there curves essentially line up, demonstrating the existence of a “threshold” temperature region at temperature above ~190 °C.

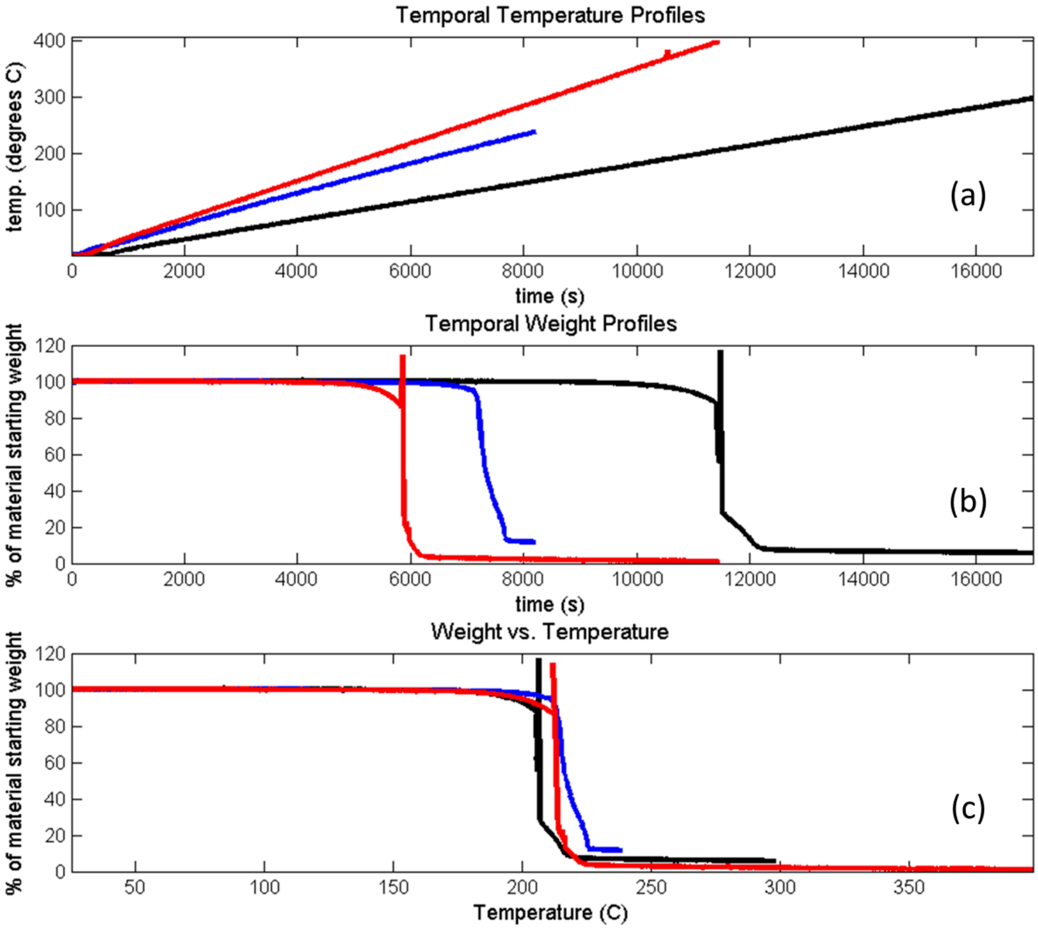

Figure1. Mass loss observed from thermal ramps. See text for details.

The other heating profile employed is simply holding the sample at a constant elevated temperature; these isotherms constitute the other half of the data set. Isotherms produce varying results based upon the temperature of the sample. Relative cool isotherm experiments show very slow decomposition, while hotter isotherms can result in rapid decomposition. As shown in panel (a) of Fig. 2, the three temperatures of 175, 185, and 195 °C span the "threshold" observed in the temperature ramp experiments. The mass loss curves in panel (b) of Fig. 2 show a very interesting relationship. The coolest isotherm at 175 °C showed less that a 10% weight loss over the time period that the other warmer isotherms were highly active over. However, this sample did eventually completely react like the others, just much more slowly. The warmest isotherm at 195 C shows a very rapid weight loss that is similar the behavior observed in the ramps. There is a complex interaction between auto-catalysis and heating rate, that leads to decomposition, so it is not possible to put a definitive temperature on the transition from slow (hours) to rapid (seconds) reaction. However, it is clear that the isotherms span this key temperature range, and the combination of the ramps and isotherms give a clear indication of the hazards of a from a CL-20 sample near 190 °C.

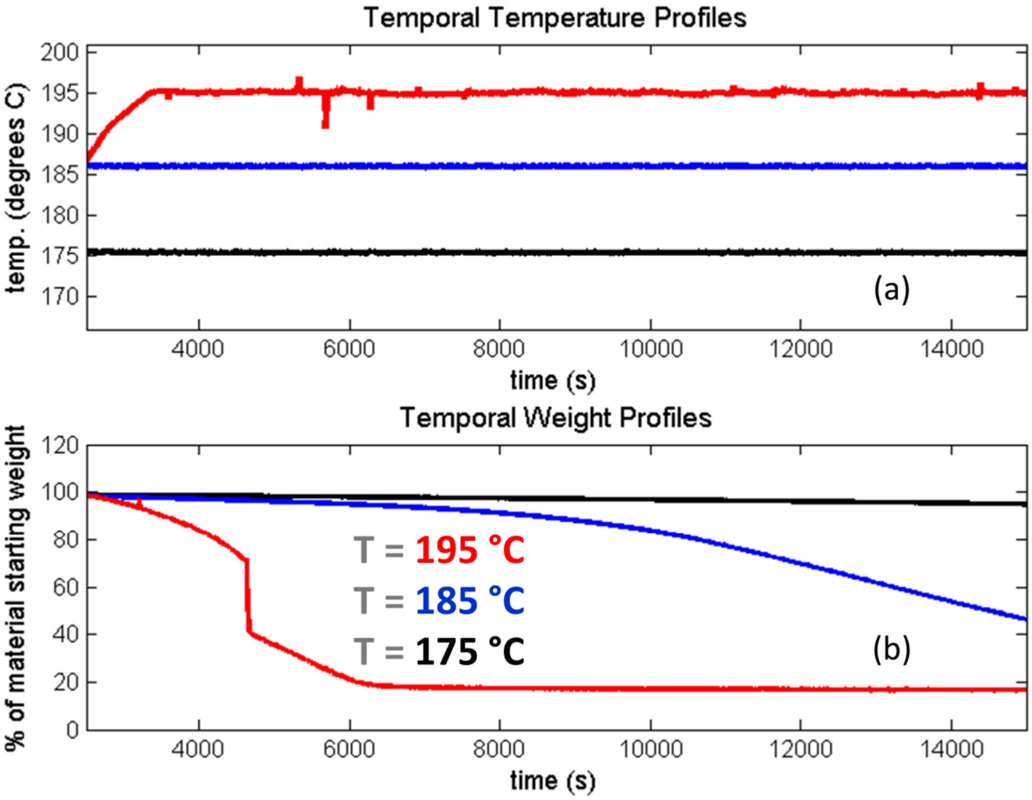

Figure2. Mass loss observed from isotherms. See text for details.

DECOMPOSITION REACTIONS: GENERAL

Upon heating, the CL-20 sample sublimes and decomposes to other chemicals. By measuring the mass spectrum of the output, the chemical composition of the products is determined. An example of the basic approach is shown in Fig. 3, below. This is the overall experiment profile for a temperature ramp. The lower panel (c) of Fig. 3 shows the familiar weight-loss and temperature ramp that the sample is subjected to. The middle panel (b) shows (in dotted black line) the sum of the signals collected by the mass spectrometer as a function of time. The upper panel (a) shows the benefit of the mass spectrometry analysis, in that it allows one to analyze a particular m/z value as a function of time. In this case, a red line is drawn on the mass-spec data to show where the temporal trace for the m/z=46 ion is extracted. The time-dependent signal intensity of this ion (multiplied by 3) is overlaid with the intensity of all the ions and it is clear there is a difference in shape. This implies that the concentrations of the chemical species are changing with time, and thus individual mass spectra are a record of this chemical change.

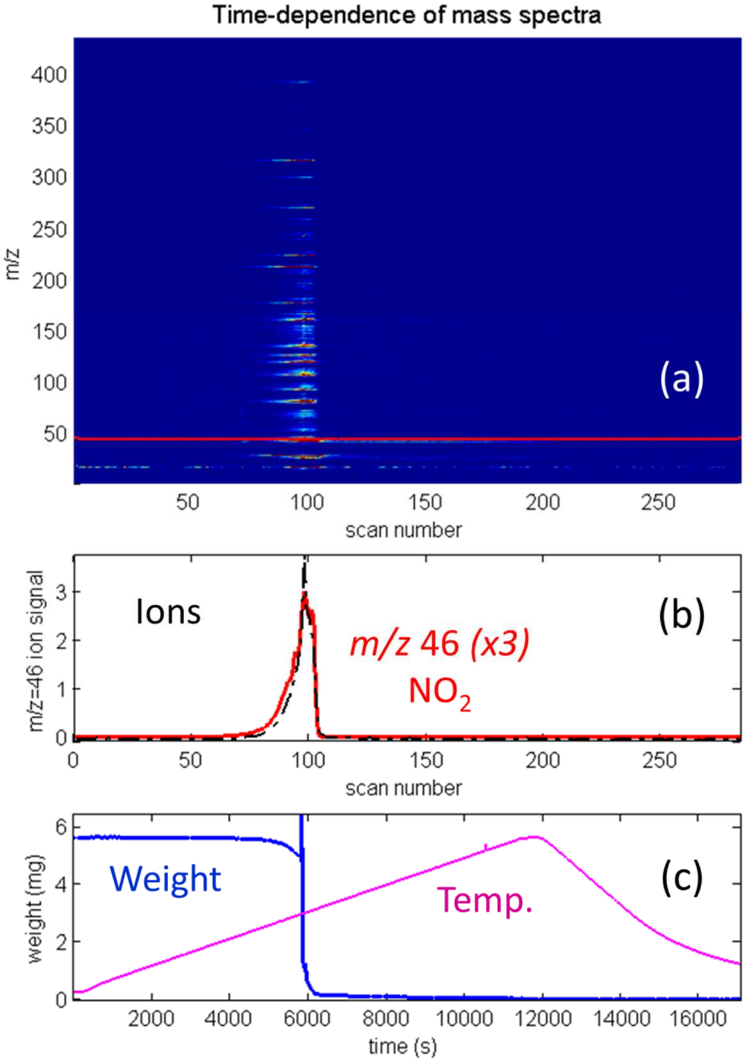

Figure3. Mass spectra recorded throughout heating profile. See text for details.

When the temporal signal intensity from each of the ions are compared, it is possible to mathematically correlate the time traces for ions with very similar behaviors. Ions that show a close temporal correlation belong to the same source or the same reaction group. An example of this analysis is shown in Fig. 4, where panel (a) shows an experimental mass spec matrix overlaid with four groups of correlated ion sets. The upper panel (a) in Fig. 4 shows (in blue) a correlated set of ions that is the group of fragments of CL-20 that are not from any reaction chemistry, but rather due to the ionization process itself. There are also reaction groups observed; the ions in the upper middle panel (in brown) evolve together because the reactive process at play is producing them simultaneously. A close look at the four panels of Fig. 4 shows subtle differences in the shape of the traces that indicates non-uniformity in chemistry. The group that constitutes the main early set of reaction products (in brown) dominates the ion signal for this experiment, these include species such as such as NO, H_2O, CO, HCN, and CO_2, many of which were also observed in the study of Turcotte *et al.* [1].

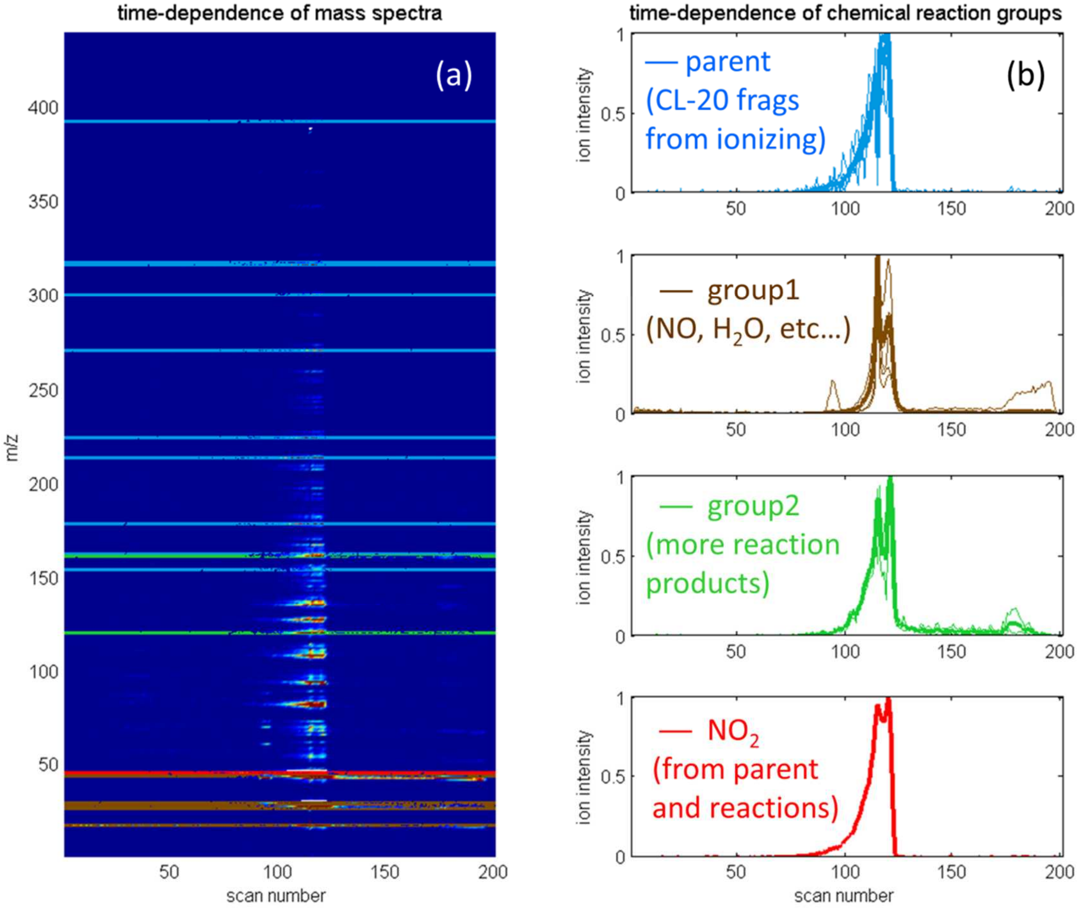

Figure4. Correlated ion groups. See text for details.

The summary of the m/z values of the various identified groups are presented in Table 2. The higher-weight molecular species represent the sublimation of the CL-20, the main reaction group is the H_2O, HCN, CO, NO, CO2, etc… set, there are some later-stage products in group2, and of course the very-abundant NO2 species. The case of the NO_2 species is quite interesting. As shown in the lowest panel of side (a) of Fig. 4, there is a very close correlation of the NO_2 ion with the CL-20 parent species. This is because a significant amount of the NO2 is due to fragmentation of the intact CL-20 upon ionization in the instrument. Thus, in order to determine to what degree the NO2 species is also being produced from reactive chemistry, we must account for this additional source term.

parent	group1	group2	NO_2
392	18	161	*46*
316	27	120	
300	28		
270	30		
224	44		
213	45		
178			
162			
154			
46			

Table 2. *m/z* values for species identified as correlated groups from CL-20 mass-spec.

For further discussion and analysis, the ions of a particular group (parent, group1, etc…) are summed up to make a representative trace for each group. These four selected groups are plotted for each experiment. As shown in Fig 5., the isotherms show a much more gradual evolution of product than the ramps, however, we observe similar overall chemistry from isotherms and ramps. Each of the three columns of Fig. 5 show the results from a different isotherm experiment. The normalized group signal is plotted in thick solid colored line along with the normalize total ion intensity in dotted black line. The un-normalized group signal is also plotted in dotted color to provide a metric of the overall abundance of each channel. Clearly seen in the all the experiments shown in Fig 5 is the different temporal order of the processes. The parent molecule begins to sublimate before any other signal is observed. The first reaction group proceeds (and completes) faster than the second, and the NO2 ion shows very similar shape to the CL-20 parent but with significant differences, particularly during the reactive chemistry of the other groups. Another clear trend in the data is the much quicker release of reaction products from the higher temperature isotherms.

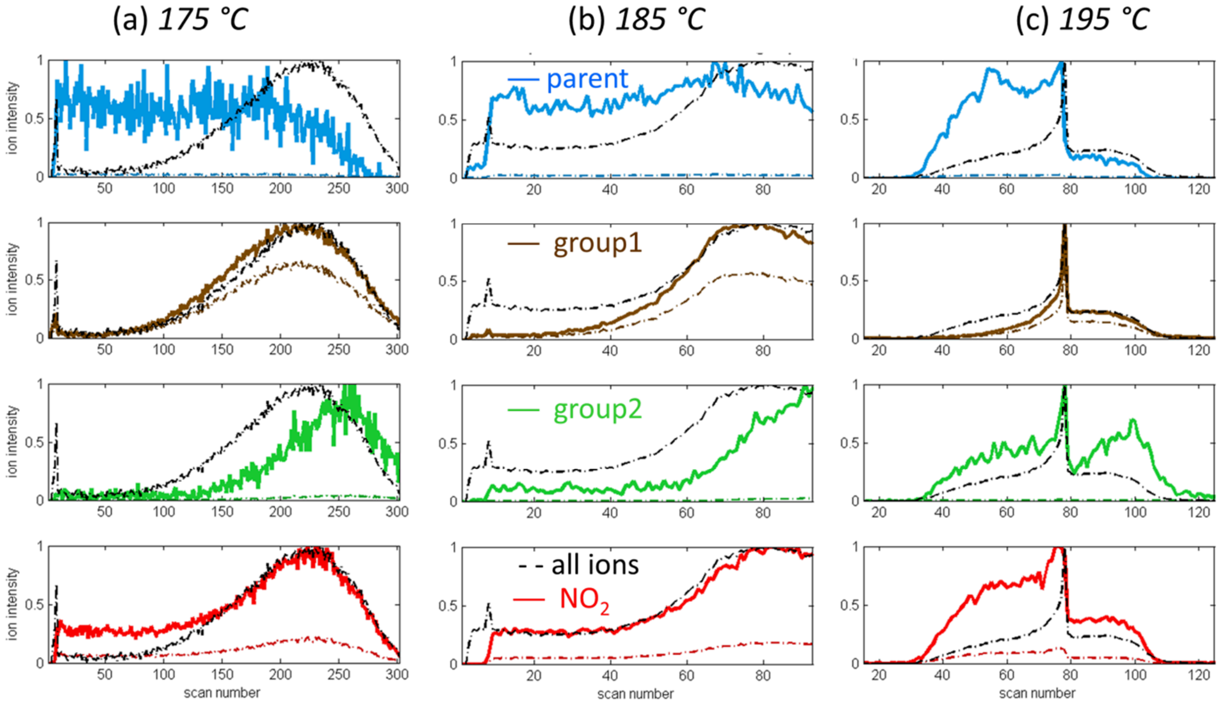

Figure5. Isothermal reaction yields. See text for details.

The same comparison between experiments is done for the heating ramps in Fig. 6, btu with a slight modification. The ramp provides a linearly changing temperature that typically affects chemistry in an exponential fashion, so examination of the log of the signal intensity is the most clear approach. As shown in Fig. 6, this approach greatly clarifies the data, as it makes the various processes stand out as shifts in the slope of the signal curves. The parent traces in the upper panels of (a), (b), and (c) of Fig. 6 all show a straight line for most of the experiment, as is expected for the signature of a simple phase change process. The reactive chemistry groups shown in the middle panels has a more complex behavior, the slope is not constant, implying a complex reaction behavior. While the NO2 signal is quite linear and closely matches the parent signal, upon inspection there is a slight curvature in the NO2 signals that is similar to the group 1 behavior. A mathematical analysis is performed to address this question.

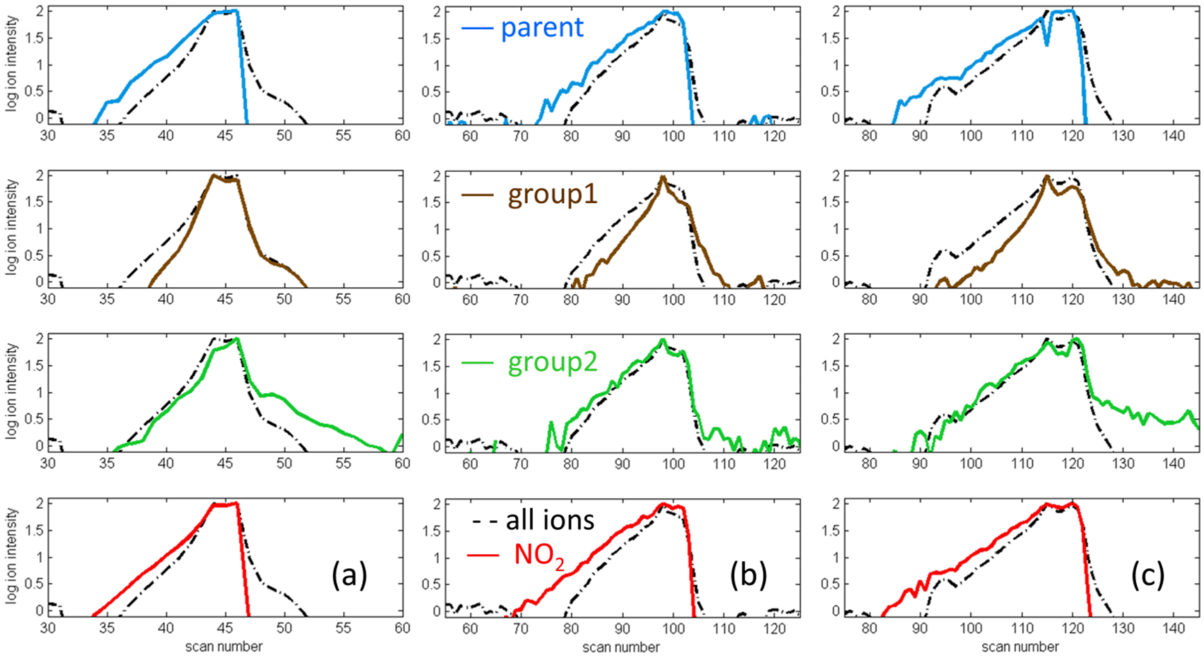

Figure6. Isothermal reaction yields. See text for details.

DECOMPOSITION REACTIONS: ROLE OF NO_2

As stated above, the NO_2 signal is comprised of multiple source terms; it comes from the CL-20 parent itself as well as the reaction chemistry. These source terms need to be analyzed in order to address the question of whether NO2 is produced directly from the sample. This analysis is carried out by comparing the NO_2 yield to the yield of all *other* parent ion species. One way to address this conceptually is to ask whether the difference between the NO_2 signal and this representation of the parent signal looks like the profile of any of the other reaction groups. The following figures display this approach applied to both the isotherms and the ramps.

The NO2 analysis for the isotherms is displayed in Fig. 7, below. The experiments are shown individually in the three two-panel graphs labeled (a), (b) and (c), The upper panels of each of these three show a direct comparison of the normalized parent signal with the normalized NO_2 signal. The difference of these two traces is shown in the panel below with the thick plum-colored line. This trace represents the degree of difference in the *shape* of the parent and NO_2 signal traces. Finally, plotted with the difference is the trace that represents the first reaction group (H_2O, CO, NO, HCN, etc…) in dotted brown color. The degree to which the difference and the group1 traces behave similarly in terms of shape is taken as evidence for the attribution of NO_2 to reactive processes.

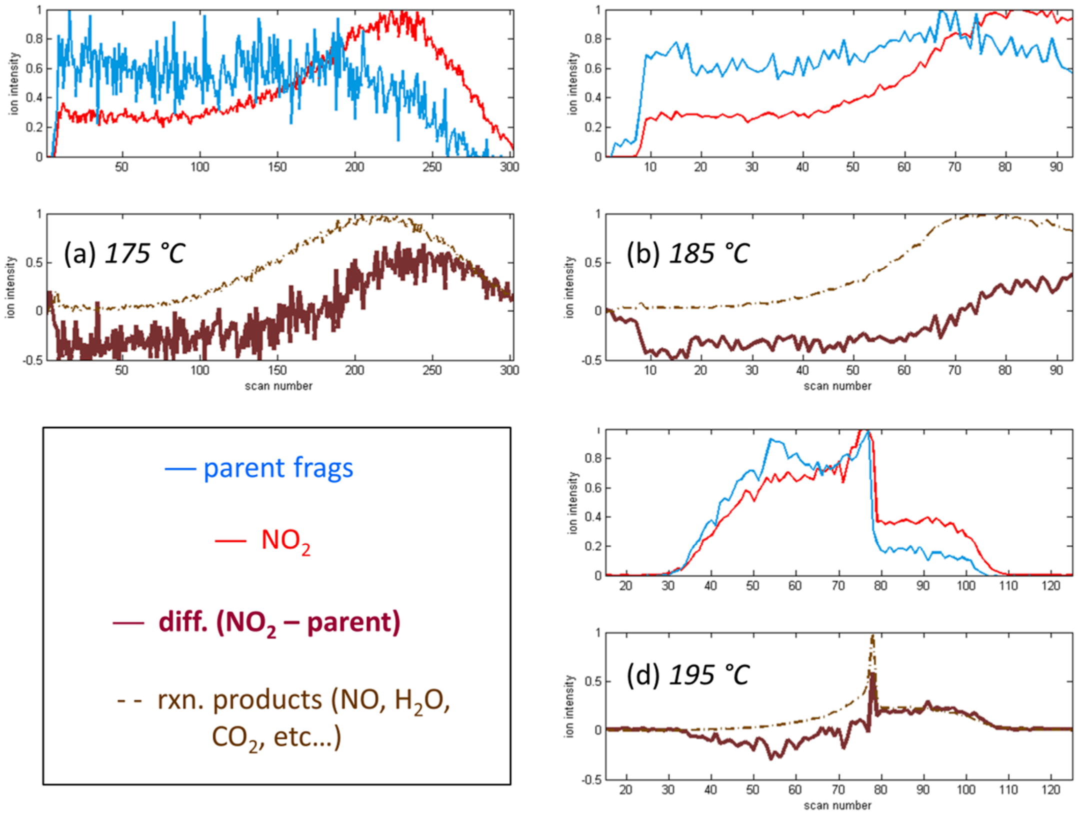

Figure7. Isothermal NO_2 yield analysis. See text for details.

This largely qualitative analysis of NO2 shown in Fig. 7 reveals a compelling trend. In all cases, during the isotherms the NO2 yield carries out to later time than the CL-20 sublimation yield, suggesting direct evolution of the gas. The temporal behavior of the "extra" NO_2 not from the CL-20 follows the shape of the reactive chemistry progress quite closely, implying that NO_2 is indeed a reaction product of CL-20. A more quantitative analysis would be fruitful in this regard.

The same NO_2 analysis approach described above is applied to the temperature ramp experiments, as shown in Fig. 8. For this set, the results do not show the same degree of consistency as the isotherms; there is indeed evidence of a difference between the NO2 yield and the parent, but it does not show the same consistent match between the NO2 and the "group1" reaction products. However, the data in panel (c) is interesting. There is a very clear match between the "extra" NO2 and the reaction products. There is a hint of this behavior in panel (b), but not definitive.

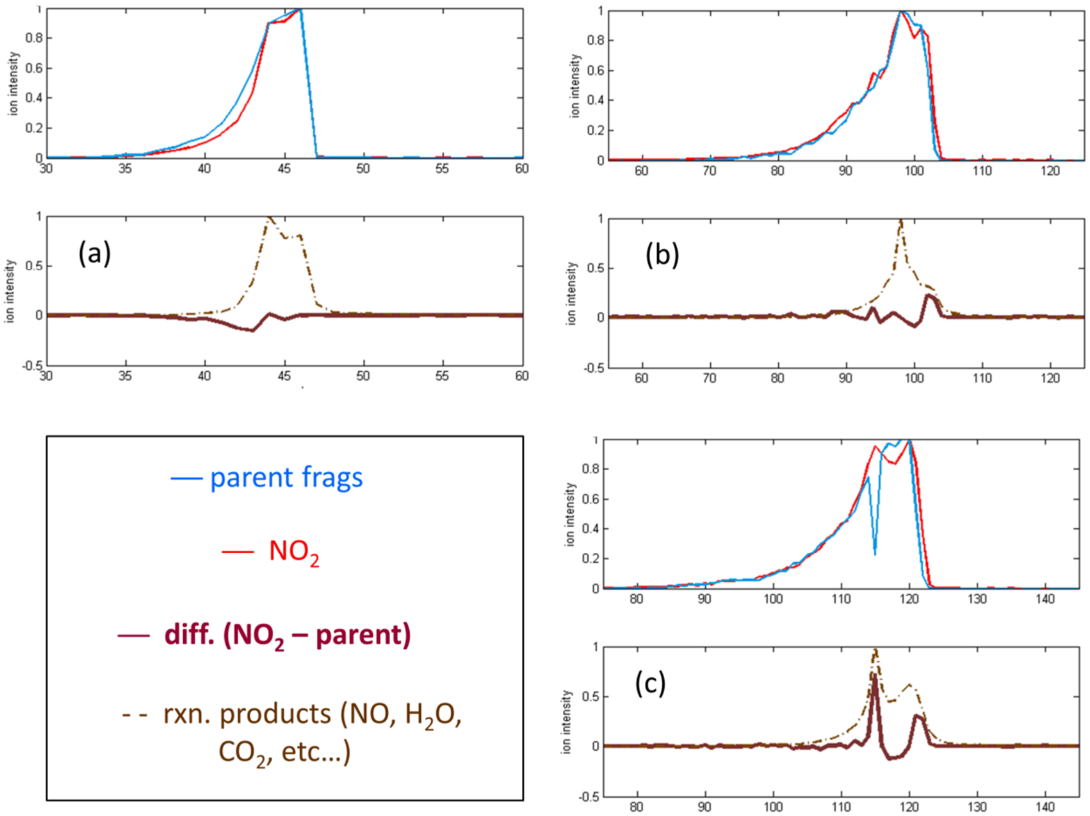

Figure8. Heating Ramp NO_2 yield analysis. See text for details.

It is clear that the NO_2 analysis presented here suggests that a certain degree of the NO_2 observed from CL-20 is due to reactive chemistry. It is not clear what the reason for the inconsistency in the temperature ramps is. One likely possibility is that the NO_2 molecule is highly reactive, and there is a complex interaction between what is produced and what is observed based upon self-interaction of the sample.

SUMMARY AND CONCLUSIONS

CL-20 shows a very rapid decomposition at temperatures above 190 degrees Celsius. The primary initial gaseous decomposition products observed are small molecules such as NO, H_2O, CO, and CO_2. NO_2 is produced directly from CL-20 ionization, so accounting for this is required to address source of observed NO_2. Analysis suggests that NO_2 is indeed directly evolved from sample but probably further reacts. Quantitative development of this approach is required as well as better time resolution in order to fully elucidate the decomposition beahior.

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